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FURTHER INVESTIGATION OF THE CHEMICAL CONSTITUTION OF THE KEROGEN OF OIL SHALES.*

By T. E. Dancy and V. Giedroyc.

Summary.

The constitution of the kerogen of the Ermelo, St. Hilaire, and Kimmeridge oil shales was studied using oxidation methods. The mechanisms of gaseous oxygen and hydrogen peroxide oxidations were investigated, and the oxidation products were compared with those obtained from alkaline permanganate oxidations. Molecular and equivalent weight determinations were made on some of the more complex products, and infra-red spectrum analysis was also used.

Introduction.

In previous work † the chemical composition of kerogens from Ermelo, St. Hilaire, and Kimmeridge oil shales was studied in detail. However, the ultimate composition could give no indication of the chemical structure of the kerogen investigated, since it consists of a mixture of an unknown number of compounds of different chemical characters.

Many chemical analyses of oil shales have been published which represent with varying degrees of accuracy the average composition of their constituents, but they can be used only for a broad classification, and do not allow the assessment of their chemical structure.

The separation of the components of the main bulk of any kerogen is at present impossible, mainly due to its small solubility in organic solvents. The only suitable methods of investigation of the chemical structure of oil shales seem to be similar to those used in researches on coal, namely controlled degradation, with subsequent separation of simpler compounds which can be identified.

Of the chemical methods used in these researches the most satisfactory are oxidation and hydrogenation, but the mechanism of the latter is too uncertain, since it involves the use of elevated temperatures. The breakdown of the organic matter of coals and oil shales by oxidation has been used extensively. In particular W. A. Bone,[1] in researches on chemical constitution of coals, developed an oxidation method employing alkaline permanganate, which was used in a modified form by Down and Himus [2] for the study of the chemical structure of a number of oil shales. They carried out " carbon balance " and " bulk oxidations " with boiling alkaline permanganate, the former consisting of the oxidation of a small amount of material under standard conditions. The oxidation products were separated into five main groups: carbon dioxide, steam volatile acids, oxalic acid, non-volatile non-oxalic acids, and unoxidized residue, and the distribution of carbon among these products gave a means of comparing different shales. In the " bulk oxidation " a considerable amount of material was oxidized and the products were isolated and identified.

* Part of a thesis for the degree of Doctor of Philosophy in the University of London.

† Dancy, T. E., and Giedroyc, V. *J. Inst. Petrol.*, 1950, **36**, 593–603.

From their experiments Down and Himus found that the constitution of some kerogens broadly resembles that of coal, since there is definite evidence of a benzenoid structure, but it is less pronounced than that in coal. In other shales (*e.g.*, Kukersite), however, no evidence of benzenoid structure was found. Further, they concluded that certain kerogens contain two types of compounds, one comparatively easily oxidized and the other highly resistant to attack. In dealing with these kerogens the use of a stage-wise oxidation was advocated. V. A. Lanin and M. V. Pronina,[3] working on similar lines, showed that prolonged treatment with alkaline permanganate of shales resistant to oxidation led to the further breakdown of the crystalline acids and increased the yield of carbon dioxide. It is, therefore, clear that some other oxidizing reagent should be sought, in particular one which would not contaminate the oxidation products by any compound unconnected with the kerogen itself.

In this work the research on the chemical constitution of Ermelo (South Africa), St. Hilaire (France), and Kimmeridge (Dorset) oil shales, started by Himus, was continued with special emphasis on the use of gaseous oxygen and hydrogen peroxide as oxidising agents.

Carbon Balance Oxidation.

Quantitative oxidations with alkaline potassium permanganate were used by Bone [1] *et al* on coals and by Down and Himus [2] on oil shales to determine both the comparative ease of oxidation of various samples and also the distribution of carbon among the products. Similar "carbon balance" oxidations were made on these three samples both before and after the removal of mineral matter by chemical means, and also on "regenerated humic acids" and water-soluble non-crystalline acids derived from the Kimmeridge. The results are shown in Table I, and the comparative rates of oxidation are plotted in Fig. 1.

Table I.

% of carbon as:	Kimmeridge.				Ermelo.		St. Hilaire.	
	Original.	Chemically enriched.	Regenerated humic acids H.I.	Intermediate non-crystal acids W.II.	Original.	Chemically enriched.	Original.	Chemically enriched.
Carbon dioxide	49·7	51·2	59·10	51·70	30·68	—	35·3	30·55
Volatile acids	8·3	8·52	0·82	0·76	5·12	—	0·2	0·2
Oxalic acid	30·9	24·88	7·71	17·01	13·24	—	6·6	8·95
Non-volatile non-oxalic acids	10·5	13·62	31·20	30·44	17·9	—	10·1	18·89
Undissolved residue	0·64	0·84	—	—	34·19	—	48·5	41·20
Time of the oxidation in hours	30	37	30	25	120	—	100	55

These results bring out very clearly the difference between the Kimmeridge, which is oxidized very easily and almost to completion, and the Ermelo and St. Hilaire, which have large portions of their kerogen apparently unattacked, even after very prolonged treatment. These residues will be referred to again.

The protective influence of the mineral matter in these shales is shown by

the somewhat increased rates of oxidation of the "enriched" samples. This effect has been described elsewhere,[4] and it should be emphasized that the differences of oxidation products obtained from the original and

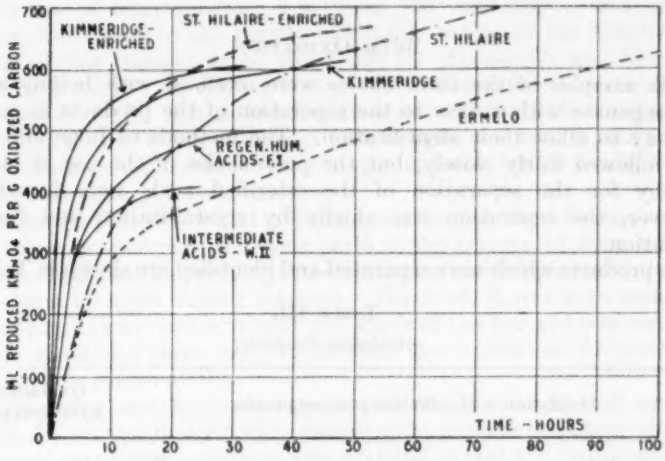


FIG. 1.

"enriched" samples should not be used to conclude that there has been a change in constitution, but may be explained by the longer times necessary for the oxidation of the former.

Further examination of the residue from the oxidation of the Ermelo showed that a large part of the algal matter had been concentrated in this part. Not only had many particles retained their radial structure observed

TABLE II.

	N.S.W. torbanite.	Oxidation residue from Ermelo torbanite.
C	84·2	81·3
H	11·9	11·0
O, N, and S	3·9	7·7
C/H	7·1	7·4
Empirical formula	$C_{15}H_{20}O_{0·5}$	$C_{14}H_{20}O$

in thin section of the original shale, but also had a much higher percentage of hydrogen than the original sample and very similar to that of the New South Wales Torbanite, which is of almost pure algal origin (Table II).[5] It is certain that the "yellow bodies" or fossil algæ in the original torbanite have resisted the attack of the oxidizing agent almost entirely, while the "black" portion (observed in thin section) has been oxidized to form soluble products. The visual identification of any particular part of the St. Hilaire in the residue was not possible owing to the very finely macerated structure of the original material, but it should be said that the

C/*H* ratio of this residue was lower than that of the original, in spite of the fact that quantities of hydrated mineral matter had certainly been concentrated in the former. Thus, it may be deduced that this residue cannot have been oxidized to any great extent.

Bulk Oxidation.

Bulk samples of the three shales were oxidized with boiling alkaline permanganate with a view to the separation of the products in sufficient quantity to allow their identification. The methods of Bone and Himus were followed fairly closely, but the possibilities of the use of chromatography for the separation of the esterified acids were investigated. However, the separation was chiefly by crystallization and fractional distillation.

The products which were separated and identified are shown in Table III.

Table III.

Oxidation Products.

Oxidation with alkaline permanganate.			Oxidation with hydrogen peroxide.
St. Hilaire.	Ermelo.	Kimmeridge.	
—	—	—	Carbon monoxide
Carbon dioxide	Carbon dioxide	Carbon dioxide	Carbon dioxide
—	—	—	Formaldehyde
—	—	—	Formic acid
Acetic acid	Acetic acid	Acetic acid	Acetic acid
Oxalic acid	Oxalic acid	Oxalic acid	Oxalic acid
—	Succinic acid	Succinic acid	Succinic acid
Benzoic acid	—	Benzoic acid	Benzoic acid (?)
o-Phthalic acid	—	*o*-Phthalic acid	—
—	—	—	*m*-Phthalic acid
p-Phthalic acid	—	*p*-Phthalic acid	*p*-Phthalic acid
Benzene tetra and penta carboxylic acids (?)	—	—	—
Mellitic acid	Mellitic acid	Mellitic acid	—

It should be emphasized that these results give but little information about the constitution of the kerogen of these oil shales, since the efficiency of the separation of the products is very low. Also a large amount of the esters in the final fractionation remained undistilled and could not be identified. This mode of oxidation was further incomplete, since it gave no information about the undissolved portions of the St. Hilaire and Ermelo and suffers from the additional disadvantage that these residues themselves were so contaminated with hydrated manganese dioxide that their separation for further study on anything but the smallest scale was impossible. Thus, it was considered that other methods of stepwise breakdown should be investigated. Two other oxidizing agents, namely gaseous oxygen and hydrogen peroxide, seemed particularly suitable, since the oxidation products obtained would be quite uncontaminated with any substance unconnected with the kerogen itself. These agents were, therefore, chosen for the further study of these samples.

Oxidation with Gaseous Oxygen.

In order to make the oxidation with oxygen take place at an appreciable rate, the use of temperatures of between 150° and 200° C was usually necessary, but owing to the readily oxidizable nature of the Kimmeridge this method was thought to be unsuitable for this sample and hydrogen peroxide was used in its further study. Initial experiments showed that the kerogen of the St. Hilaire and Ermelo were very little affected by temperatures up to 250° C out of contact with oxygen, and thus it was certain that any break-down in contact with oxygen at below 200° C would be true oxidation and not a pyrolytic reaction.

It was hoped that this would prove a convenient method for the separation of larger quantities of the same parts of the kerogen of these samples which were resistant to permanganate oxidation and which could then be broken down by more violent reagents. However, it was soon seen that by prolonging the oxidation, almost the whole of the kerogen was rendered soluble in alkali, and there was no indication that oxidation of a particular part took place preferentially.

The apparatus used for these experiments was similar to that used by Donnelly, Foott, and Reilly [6] when studying the gaseous oxidation of coals. This type of circulating apparatus was modified so that the consumption of oxygen throughout the reaction could be followed continuously, together with the evolution of CO, CO_2, and water.

The Ermelo and the St. Hilaire behaved similarly to coals in the manner in which the amount of organic matter converted to alkali-soluble products increased with time of oxidation, and also in the way that the rate of consumption of oxygen decreased faster than the rate of evolution of CO and CO_2. Further it was noted that at the beginning of an oxidation, the absorption of oxygen was rapid, and there was a short interval before gaseous products commenced to be evolved. Further relevant results from these oxidations are seen in Table IV.

Table IV.

Oxidation with Gaseous Oxygen.

	Ermelo torbanite.		St. Hilaire oil shale.
	150° C.	200° C.	200° C.
Time, hrs	220	200	90
Total O_2 used/g orig. C, ml	463	1152	925
Oxygen saturation stage, g (O_2/g C)	0·57	1·34	1·29
C in CO_2, %	5·6	23·0	14·1
C in CO, %	2·6	11·0	5·2
C in residue, %	90·6	65·5	80·7
H in H_2O, %	45·8	69·8	78·5
H in residue, %	54·1	30·3	25·0
Vol C/Vol H	1·73	4·85	2·36
Increase in oxygen in residue, %	2·64	8·34	5·12
Humic acids, %	13·9	44·0	18·7

Oxidation Residues.

A stagewise oxidation of the Ermelo was performed, during which samples of the oxidized kerogen were removed, and these were extracted separately with 1 per cent sodium hydroxide solution. From these solutions, regenerated humic acids, which were similar to those obtained from coals, could be precipitated. It was found that the composition of the acids obtained from the earlier part of the oxidation was very similar to those from the later stages (Table V). Further evidence of the very different mechanism of this oxidation from that with permanganate was given by the results of oil yield experiments.

Table V.

	0–175 hr.	175–225 hr.
Carbon	64·21	64·42
Hydrogen	3·13	3·15

Determinations were made on the original kerogen, on the residue from the permanganate oxidation, and the kerogen remaining undissolved by alkali after each stage of the oxygen oxidation. An apparatus was developed for the estimation of oil yields from the small samples (about 1 g) available,[7] and the results are shown in Table VI. It is seen that the yield

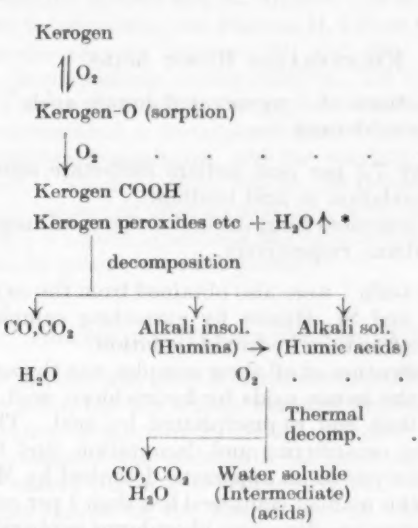
Table VI.

	Original.	Permang. oxn. res.	Oxygen oxn. res. after X hr oxidation at 150° C.				
			45.	75.	100.	175.	225.
Carbon . .	79·8	81·3	79·25	78·1	77·2	75·1	73·6
Hydrogen .	7·2	11·0	6·10	5·40	4·72	4·00	3·71
g Oil/g C . .	0·433	0·862	0·26	0·15	0·10	0·07	0·04

of oil per gram of carbon from the permanganate oxidation residue was nearly twice that of the original kerogen, supporting the view that this residue consisted of almost pure and essentially unchanged algal remains (cf. Table II). The oil yields on the oxygen oxidation residues on the other hand showed that the insoluble part of the oxidized kerogen had been greatly affected. For an increase of C/H from 11·0 to 13·0 there had been a decrease of oil yield of 40 per cent, and thus it may be concluded that this mode of oxidation had a profound effect on the kerogen as a whole, and even after 225 hours the oxidation was not complete, though after this time more than 60 per cent of the carbon had been rendered soluble in alkali. The regenerated humic acids themselves yielded negligible oil up to 600° C, but CO, CO_2, and water were evolved.

The chief products from the oxidation of both these shales were "regenerated humic acids"; however, these evidently decomposed slowly to water-soluble products, since such material was only obtained from the

oxidized kerogen if heating was continued for a long period after the consumption of oxygen became negligible. The further study of the "regenerated humic acids," which will be described later, is clearly of importance, since they appear to be one of the primary breakdown products of the kerogen. A tentative mechanism for this degradation is suggested below, and the relative rates of the various reactions are introduced to explain the accumulation of "humic acids."



* Jones, R. E., and Townend, D. T. A. *Trans. Faraday Soc.*, 1946, **42**, 297.

Oxidation with Hydrogen Peroxide.

It has been mentioned that oxidation by hydrogen peroxide was considered suitable for the further study of the Kimmeridge oil shale, and some initial experiments were made to determine the concentration and temperature best suited to the reaction. These showed that boiling 5 per cent H_2O_2 rapidly converted nearly all the kerogen to CO_2, while in the presence of alkali the auto-decomposition of the peroxide was rapid and therefore the reaction with the kerogen was much slower, yielding non-crystalline acids. It was found that in order to obtain the maximum yield of non-gaseous oxidation products the reaction had to be conducted in stages at a temperature not higher than 75° to 80° C. Two large-scale (200 g kerogen) oxidations in acid and alkaline medium of the partially "enriched" shales (7 to 8 per cent ash) were performed under these conditions. By the intermittent removal of oxidation products after each addition of 100 to 200 ml of 100 vol H_2O_2, a range of humic and other intermediate acids was obtained. A small amount of crystalline end products was also separated, and some of the individual components were identified. Table III shows these alongside those obtained from the permanganate oxidation of the same shale. Carbon monoxide, formaldehyde, and formic acid were peculiar to

the hydrogen peroxide oxidation, and the last two compounds, which would be oxidized to CO_2 by permanganate, were only found in this instance owing to their intermittent removal. There is a similarity between the oxidation of carbonaceous materials with oxygen and hydrogen peroxide in the formation of humic and other intermediate acids as the main products, and since no study of these substances obtained from oil shales had been made, particular attention was paid to them.

Regenerated Humic Acids.

Three different fractions of "regenerated humic acids" were isolated from the Kimmeridge oxidations:—

H. I extracted by 7·5 per cent sodium carbonate solution from the residue after oxidation in acid medium.
H. II and H. III separated from the first and second stages of oxidation in alkaline medium, respectively.

"Regenerated humic acids" were also obtained from the oxygen oxidation of both the Ermelo and St. Hilaire by extracting samples of oxidized kerogen with 1 per cent sodium hydroxide solution.

The method of purification of all these samples was the same; after the first precipitation of the humic acids by hydrochloric acid, they were re-dissolved in dilute alkali and re-precipitated by acid. They were then thoroughly washed by centrifuging and decantation, and finally purified by prolonged electrodialysis in an apparatus described by Marsden.[8] The products obtained in this manner contained less than 1 per cent of inorganic impurities. Final drying was done over phosphorus pentoxide in a vacuum desiccator; the chemical analyses and other experimental results are shown in Table VII.

Table VII.

	Kimmeridge.						Ermelo.		St. Hilaire.	
	Kero-gen.	H.I.	H.II.	H.III.	W.I.	W.II.	Kero-gen.	r.h. acids.	Kero-gen.	r.h. acids.
Carbon	68·82	63·79	66·40	64·95	60·35	51·20	79·8	65·00	84·50	64·00
Hydrogen	7·20	6·16	6·42	6·29	5·71	3·94	7·16	3·17	7·29	2·38
Nitrogen	1·43	0·86	1·14	1·15	1·12	2·18	1·57	1·34	1·27	1·63
Sulphur	9·41	3·61	7·67	6·77	8·12	4·85	0·60	0·62	1·07	1·09
Oxygen	13·14	25·58	18·37	20·84	24·70	37·83	10·87	29·80	5·87	30·90
Equiv. wt. electrometric titration	—	202	—	—	—	—	—	244	—	190
Equiv. wt. calcium acet. reaction	—	395	400	489	287	—	—	—	—	—
Gr. equiv. of methoxyl	—	393	397	488	—	—	—	—	—	—
Molecular wt in catechol	—	400	400	354	260–340	—	—	232	—	198
C/H	9·56	10·35	10·30	10·30	10·55	13·55	11·14	20·5	10·85	26·90

While the acids from the Ermelo and St. Hilaire were easily soluble in dilute alkali and seemed to behave as stable compounds, the acids from the Kimmeridge, after drying, could be completely re-dissolved only by boiling alkali, and at the same time suffered some decomposition to water-soluble products.

Equivalent Weight Determination.

Electrometric titration was used to determine the equivalent of one-COOH in " regenerated humic acids " obtained from coals. In this work a Marconi-Ecko pH meter with a glass electrode was used to determine the end point of a back titration, with standard hydrochloric acid, of the humic acids dissolved in excess alkali. Reproducible results were easily obtainable on the acids from the Ermelo and St. Hilaire, 120 and 121 for the former and 196 and 192 for the latter, but fraction H. I from the Kimmeridge gave inconsistent results varying between 200 and 400. This was no doubt caused by the decomposition during solution, but by standardizing conditions most of the values fell in the region of 200. Nevertheless, since this probably represented a decomposed form of the acids, this titration method was considered unsuitable, and the reaction with calcium acetate was used instead.[9] To check these results, the determination of methoxyl groups was made before and after methylation with diazomethane. As can be seen in Table VII a good agreement was obtained, and this also furnished proof that phenolic groups were not present.

Molecular Weight Determination.

A cryoscopic method was used in the determination of molecular weight of these humic acids, but since they were not soluble in any of the usual cryoscopic solvents, a solution in molten catechol was employed. The experimental procedure was essentially the same as that used by Smith and Howard,[10] except that a lower concentration (0·5 to 1·0 per cent) was used. Again the results for the Ermelo and St. Hilaire were consistent, about 232 and 198 respectively, while the acids from the Kimmeridge showed large variations in values; however, some average molecular weights obtained from many experiments are quoted in Table VII.

It must be pointed out that the " regenerated humic acids " H. II and H. III behaved differently from those obtained in acid medium, being much less stable than the latter. After boiling with water or after standing in air at room temperature they were partly oxidized to products soluble in alcohol or water. Also a large proportion of H. III, after prolonged extraction with alcohol, either dissolved or dispersed in it, but after their recovery from the solution by evaporation they could not be easily re-dissolved. This suggested that they possessed polymeric properties, but the reaction could not be considered pure polymerization, since it was accompanied by a change in composition.

Water-soluble Non-crystalline Oxidation Products (from Kimmeridge).

The solution of water-soluble oxidation products, which remained after the precipitation of " regenerated humic acids," was evaporated on a water-bath. During this process a black resinous material separated out, which was isolated and purified by electrodialysis. When dried it was a brittle black lustrous substance and became insoluble in water, but was

still soluble in alcohol. Efforts were made to resolve this fraction " W. I " (Table VII) into its ultimate components by chromatography, but the results were negative, since both alumina and silica adsorbed the substance

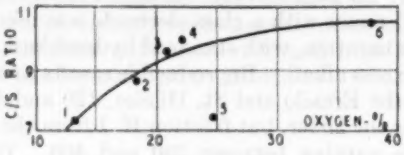


FIG. 2.

	$\%O_2$.	C/S ratio$_2$.
1. Original kerogen	13·14	7·32
2. Reg. humic acids I	18·37	8·65
3. Reg. humic acids II	20·84	9·60
4. Reg. humic acids II (fraction soluble in alcohol)	22·14	10·00
5. Intermediate acids, W.I.	24·70	7·43
6. Intermediate acids (fraction soluble in water)	37·83	10·50

so strongly that prolonged elution with methanol and hot water produced no development. However, this cannot be used as evidence of the homogeneity of the material.

It was noticed that the hydrogen peroxide oxidations gave a range of

TABLE VIII.

Fraction " W. I " of Non-crystalline Acids.

Region of spectrum, cm^{-1}.	Assignment.	Remarks.
1830 1805 1780	C=O carbonyl in anhydrides	Acids anhydrides usually show a double band: one between 1850 and 1800 cm^{-1} and the other between 1800 and 1750 cm^{-1}. Thus, the presence of anhydride structure is possible.
1740	C=O ester carbonyl	Usual frequencies between 1750 and 1725 cm^{-1}.
1695	C=O carbonyl in acids	Usual frequencies 1700 and 1670 cm^{-1}, but presence of aldehyde or keto groups is not excluded, since their frequencies lie between 1725 and 1690 cm^{-1}.
1540 1505	Probably some substituted aromatic ring	No definite assignment could be made.
1435 1370	CH_2 CH_3	C–H deformation frequencies.
1265	C–H single bond	In esters; possibly phthalate.
1205	C–O single bond	From 1150 to 1250 cm^{-1} methyl esters of higher fatty acids.
1065 1040	C–O single bond C–O single bond	
945 865	C=C bond C=C bond	These frequencies are associated with deformational modes of C–H bonds attached to C=C bond.

products in which the increase in oxygen content followed the decrease in sulphur. Fraction "W. I" was an exception, since it had an unusually high percentage of both oxygen and sulphur (Fig. 2), and thus may be assumed to have been derived from a part of the kerogen particularly rich in sulphur.

Fraction "W. II" (Table VII) was obtained by the extraction with methanol of the dried oxidation products from which crystalline acids had previously been removed by treatment with ether and acetone. This extract was dark reddish-brown in colour, and after the evaporation of the

TABLE IX.

Intermediate Non-crystalline Acids Obtained in Acid Medium.

Region of spectrum cm^{-1}.	Assignment.	Remarks.
1720	C=O ester carbonyl	Usual frequencies 1750–1725 cm^{-1}, but conjugation tends to lower the characteristic frequencies.
1695	C=O carbonyl in acids	The presence of aldehyde and keto groups possible.
1610	C=C aliphatic conjugated	Usual frequencies for C=C, 1660–1640 cm^{-1}, but in aliphatic conjugation it occurs near 1600 cm^{-1}.
1565	Substituted benzene ring possible	No definite assignment could be made.
1490 1435 1410	CH_2 CH_3 CH	C–H deformation frequencies.
1265	C–O single bond	In esters could be phthalate.
1205	C–O single bond	From 1250 to 1150 cm^{-1} methyl esters of higher fatty acids.
1050	C–O single bond	Could be alkyl ether.

solvent yielded a dark very viscous oil. This was re-dissolved and methylated with diazomethane. During this reaction a heavy precipitate was formed, which when separated and analysed proved to be identical with "W. I" after methylation (C = 64·65 per cent, H = 6·12 per cent). The methyl esters of the intermediate acids were freed from solvent, dried, and distilled under reduced pressure (45 mm Hg), but the distillation was stopped when the temperature of the distillate reached 90° C, owing to the rapid decomposition of the esters in the flask.

The six fractions collected were all clear liquids with very unpleasant smells, characteristic of mercaptans or thioethers, and all were free from nitrogen but contained sulphur. Further proof of the presence of mercaptans was obtained by characteristic reactions. The precipitated mercuric compounds had no fixed melting points, and the determination of boiling points also indicated that no fraction represented a single compound, but

the low boiling points of the fractions suggested that aliphatic compounds were predominant. After standing, small amounts of crystalline compounds were found in the last two fractions; these were probably methyl esters, and the presence of esters in fraction 6 was later confirmed by its infra-red spectrum (Table XI). This spectrum also confirmed the presence of unsaturated aliphatic compounds. The residue left in the distilling flask

TABLE X.

Esters of Intermediate Acids; Obtained in Alkaline Medium ("W. II").

Region of spectrum cm^{-1}.	Assignment.	Remarks.
3300	O–H with hydrogen bonded to some other atom	Presence of N–H groups is not excluded.
1740	C=O ester carbonyl	
1650	C=C	In simple olefin.
1605	C=C aliphatic conjugated	
1460	CH_3	C–H deformation frequencies.
1385	CH_3	
1240	C–O single bond	Could be alkyl-aryl ether, esters, and anhydrides.
1115	C–O single bond	Could be alkyl ethers, phthalate also possible.
1055	C–O single bond	
1015	CH_3	
965	C=C	965 cm^{-1} was found in olefines of the type R′CH=CHR″.
785	Meta-substituted benzene ring	
730	Monosubstituted benzene ring	Benzene ring vibrations. Also found in paraffins with methyl groups attached along the chain.
685	C–S ? C=C ?	600–700 cm^{-1} C–S valency vibrations in benzene ring.

was a brittle dark solid insoluble in organic and inorganic solvents, and the presence of carbonized material indicated that the esters of the "intermediate acids" had been decomposed during the distillation, and the mercaptans and other unsaturated aliphatic compounds in the distillate were products of this decomposition.

INFRA-RED SPECTRUM ANALYSIS.

To obtain more information about the chemical structure of these intermediate non-crystalline acids, infra-red spectra of some of the products were made. The results are tabulated in Tables VIII, IX, X, and XI, and Fig. 3.

The empirical correlation between the observed absorption bands and molecular structure could not be considered as definite. However, according to the literature,[12, 13] frequencies above 1350 cm^{-1} allow fairly correct assignments. Thus the following chemical groups are almost certainly present : $-OH$; $-C{=}O$; $-C{=}C-$; $-C{=}C-C{=}C-$ in aliphatic compounds and aromatic rings ; CH ; CH_2 and CH_3. Since the general level of absorption of some of the spectra was high, some of the weaker bands might have been masked, and thus the presence of further groups might have escaped detection.

TABLE XI.

The Fraction N6 of Vacuum Distillate of Methylated Intermediate Acids Obtained in Alkaline Medium.

Region of spectrum cm^{-1}.	Assignment.	Remarks.
1740	C=O ester carbonyl	
1650	C=C double bond	Simple unsaturated aliphatic hydrocarbon.
1620	Aromatic ring	Could be associated with the presence aromatic material.
1445 1370	CH_2 CH_3	C-H deformation frequencies.
1275	C-O single bond	In esters, could be phthalate.
1220 1170	C-O single bond C-O single bond	From 1150 to 1250 cm^{-1} methyl esters of higher fatty acids.
1030	C-O single bond	
860	C=C double bond	This frequency is associated with deformational modes of C-H bonds attached C=C bond.
780	Meta-substituted benzene ring	
690	C-S ? C=S ?	600–700 cm^{-1} C-S valency vibrations. In benzene ring.

DISCUSSION OF RESULTS AND CONCLUSIONS.

The alkaline permanganate oxidations clearly demonstrated the very different type of kerogen possessed by the Kimmeridge oil shale, as compared with that of either the Ermelo or St. Hilaire. Nearly the whole of the first shale oxidized to soluble products, and the very small residue (ca. 1 per cent) was clearly identifiable as consisting of remains of spore exines (also identified in thin section of the original shale). However, a large part of the kerogen of both the Ermelo and St. Hilaire remained undissolved even after prolonged permanganate oxidation. The oxidation residue from the former was light brown in colour and had a composition very similar to that of the New South Wales algal shale, and also gave a

very high oil yield. This evidence, together with visual identification of many "yellow bodies" in the residue, suggested that it consisted almost entirely of unchanged algal remains. Thus, it appeared that the oxidation had caused the main black matrix of the shale to be preferentially attacked, leaving a residue of unaltered yellow algal particles. Since the St. Hilaire is derived from very finely macerated material, visual identification of components concentrated in the oxidation residue was not possible, but it was found that the yield of oil per gram of carbon from the residue was

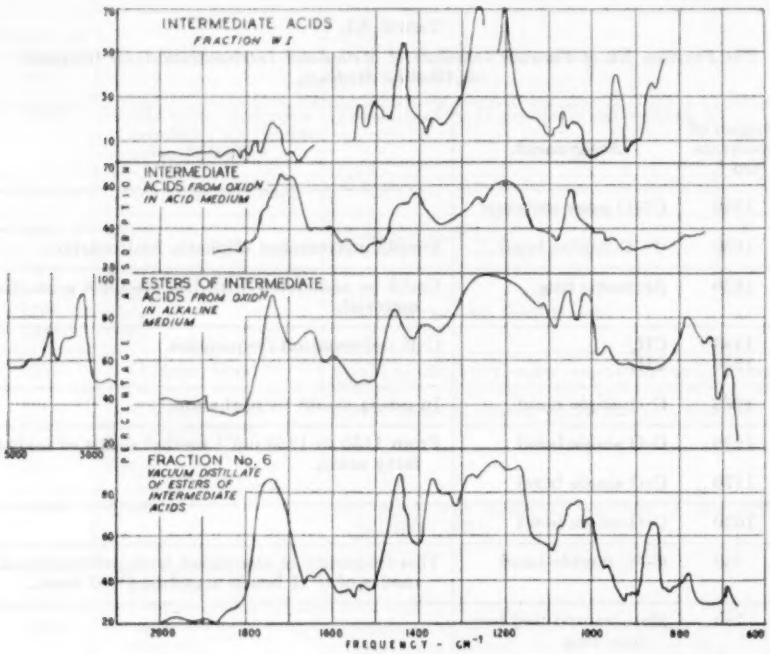


FIG. 3.

greater than that of the original shale and also its C/H was lower. Thus, it could be concluded that permanganate oxidation caused similar components to be concentrated from both shales.

A number of benzene carboxylic acids were identified in the products from bulk permanganate oxidations of the Ermelo and St. Hilaire, and there was little evidence of the presence of complex aliphatic acids. The main difference between the oxidized part of the kerogen of the two shales was the lack of acetic acid from the St. Hilaire.

Oxygen oxidation was unsuitable for the isolation of these oxidation residues for study by other methods, since there was apparently no preferential attack of any portion of the kerogen. This may be judged from the constancy of the chemical composition of the "regenerated humic acids" obtained during the process. However, the large quantities of these acids obtained from the two shales were shown to have very similar compositions

to similar humic acids obtained from coals but with somewhat higher C/H ratios (Table XII). Apart from these main products and CO, CO_2, and water, a very small quantity of water-soluble intermediate acids was obtained, but these appeared only after very prolonged oxidation, and were evidently decomposition products of the "humic acids." The residues remaining after the humic acids had been extracted from the oxidized kerogen were found to be highly oxidized themselves, and consequently yielded very much less oil, and were therefore unlike the permanganate oxidation residues.

Hydrogen peroxide oxidation, used on the much more easily oxidized Kimmeridge, was found to be very suitable for the preparation of a range of products from highly complex "regenerated humic acids" of varying degrees of oxidation, to somewhat similar non-crystalline alcohol- and water-soluble acids. Crystalline acids were also obtained, but the yield

TABLE XII.

Source of regenerated humic acids.	Composition, %.					C/H.
	C.	H.	N.	S.	O.	
Kimmeridge oil shale. Oxid with H_2O_2 in acid medium H.I.	63·79	6·16	0·86	3·67	25·58	10·35
Kimmeridge oil shale. Oxid with H_2O_2 in alkaline medium H.II	66·40	6·42	1·14	7·67	18·37	10·35
and H.III	64·95	6·29	1·15	6·77	20·84	10·32
Ryder dull coal. Oxid with H_2O_2 [11]	65·0	3·3	1·4	0·6	29·7	19·70
Ermelo torbanite. Oxid with O_2 gas	65·0	3·17	1·34	0·69	29·8	20·5
St. Hilaire oil shale. Oxid with O_2 gas	64·0	2·38	1·63	1·09	30·9	26·9
Parkgate bright coal. Air oxid at 150° C [11]	70·3	3·2	1·6	0·9	24·0	22·0

was small; nevertheless, the presence of benzenoid acids established the existence of benzenoid structures in the kerogen. However, there was ample evidence that an aliphatic structure predominated, since there was only a small yield of non-volatile (except oxalic acid) acids from the permanganate oxidation. A large yield of these acids is usually associated with a predominantly benzenoid structure. Infra-red absorption spectra of intermediate acids from the H_2O_2 oxidations showed the presence of aliphatic unsaturation (especially conjugated dienes), and so the original kerogen could be expected to be even more unsaturated. This may account for the very easily-oxidizable nature of the Kimmeridge, and also the tendency of the intermediate acids to polymerize.

It may be suggested that the low carbon/hydrogen ratio in the Kimmeridge kerogen is due to the presence of saturated aliphatic side chains, but the same could not apply to the regenerated humic acids. A permanganate "carbon balance" oxidation of the latter give a tenfold smaller yield of acetic acid than that of the original kerogen, and since acetic acid is thought to be derived from side chains, it was to be expected that the humic acids should have a much higher C/H ratio than the kerogen.

However, the increase was only from 9·6 to 10·35, and therefore the humic acids must be of essentially aliphatic structure. The marked differences of C/H ratios of the humic acids from the Kimmeridge and those from the Ermelo and St. Hilaire are well illustrated in Table XII. The composition of similar acids derived from coals by the same methods of oxidation are also shown.

The low values for the molecular weights of the regenerated humic acids from the shales investigated were incompatible with their properties, but this could be explained if it is assumed that dissociation takes place in the highly polar solvent (catechol). Therefore the values obtained in catechol did not represent the actual molecular weights of regenerated humic acids, but indicated the order of the average size of the units from which they are built.

The high sulphur content is the characteristic feature of the kerogen from the Kimmeridge shale. In the alkaline permanganate oxidation, sulphur was not found as a component in any organic end-product. This led Down to suggest that sulphur was present in the kerogen as side chains or in heterocyclic rings also containing oxygen.[14] However, oxidation with H_2O_2 gave a whole range of products in which sulphur was present in organic combination. Since, during the oxidation, side chains were mostly removed, sulphur present in their structure would also have been oxidized. The fact that it is still present in the water-soluble intermediate acids, which when distilled in vacuum at a comparatively low temperature yielding a mixture of mercaptans, suggested that at least part of sulphur was in the nuclear structure of the kerogen.

The main conclusions from the above work may be summarized as follows :—

1. The Ermelo torbanite contains algal material very similar to that found in the New South Wales torbanite. The remainder of the kerogen consists of humic material, basically benzenoid in structure, similar to that found in bituminous coals.

2. The St. Hilaire kerogen also consists of two distinct types. The part more easily oxidized by permanganate was similar to that in the Ermelo, but was probably more condensed with fewer side chains. The humic acids obtained were again similar to those derived from coals. The kerogen resistant to permanganate oxidation may be of partly algal origin, since its yield of oil was higher than that of the original shale.

3. The Kimmeridge is peculiar in its ease of oxidation and high sulphur content. It seems to contain mainly unsaturated aliphatic or cyclic structures, but the presence of benzenoid substances in small quantity was also proved. The origin of the sulphur is unknown, but certainly occurs in the main kerogen structure in stable combination, possibly replacing oxygen. The kerogen as a whole is certainly very different from that found in most carbonaceous materials.

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RING ANALYSIS OF HYDROCARBON MIXTURES.

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Summary.

Methods are developed using only refractive index and molecular weight for estimating the average number of rings per molecule, the average number of carbon atoms occurring in ring structure, the average weight per cent rings, and the average weight per cent carbon in ring structures for hydrocarbon mixtures consisting of naphthenes and paraffins or of aromatics and paraffins. Application of these four methods to 722 pure hydrocarbons (paraffins, naphthenes, and aromatics) shows that the average algebraic deviations between calculated and theoretical values is +1·5 weight per cent rings, + 0·02 rings per molecule, + 0·09 ring carbon atoms per molecule, and + 0·06 weight per cent ring carbon atoms.

Symbols Used in Derivation of Equations.

B.P. = boiling point in ° F at 760 mm.
C_A = number of carbon atoms occurring in aromatic rings.
C_N = number of carbon atoms occurring in naphthene rings.
M = total molecular weight of compound or mixture.
M_A = molecular weight of aromatic ring portion.
M_N = molecular weight of naphthene ring portion.
m = slope of line relating refractive index of a given hydrocarbon series with the reciprocal of molecular weight.
n = total number of carbon atoms per molecule.
n_D^{20} = refractive index at 20° C using sodium D light.
R_A = number of aromatic rings per molecule.
R_N = number of naphthene rings per molecule.
x = series constant in general formula C_nH_{2n+x}.

Introduction.

The quantitative separation of individual hydrocarbons from petroleum fractions is a difficult problem which at the present time has been solved only for the relatively low-boiling fractions. As the molecular weight of the components of kerosines, gas oils, and lubricating oils increases, the number of possible isomeric hydrocarbons also increases enormously, and the usual processes of fractional distillation, crystallization, extraction, adsorption, etc., are of limited usefulness in resolving the fractions into individual hydrocarbons because of their lack of sensitivity for separating isomers of similar homologous series and because of the probable low concentration of any individual hydrocarbon of definite structure.

For these reasons, determinations of various classes of hydrocarbons (paraffins, naphthenes, and aromatics) or sub-classes of hydrocarbons (benzenes, diphenyls, naphthalenes, etc.), or determinations of the average proportions occurring in ring structures are of considerable importance towards increasing the knowledge regarding the chemical composition of the higher-boiling petroleum fractions. Sachanen [12] points out that the commercial value of most petroleum products is governed rather by their

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bulk chemical composition than by the structure of specific individual hydrocarbons. For example, motor oils with high content of aromatics may be expected to have a low viscosity index; gasolines with high content of aromatics and highly branched paraffins are likely to have a high octane number, etc.

Some of the methods proposed for estimating the classes of hydrocarbons present or the average number of carbon atoms occurring in ring structures have been reviewed by Sachanen.[12] A common procedure for determining the proportions of aromatic and naphthene rings and paraffin chains in lubricating oils is that proposed by Vlugter, Waterman, and Van Westen,[16] but this method is rather cumbersome to use, gives wide deviations when applied to pure hydrocarbons,[13] and has limited application to gas oil and kerosine fractions. It does have the advantage of being useful for estimating the composition of overall straight-run or treated distillates; most empirical methods require that aromatics be first removed for application of the analytical scheme to the saturated portion.

With separation of the petroleum fraction into aromatic and paraffin–naphthene portions by such a process as silica-gel adsorption, an estimation of the proportions of ring- and chain-type hydrocarbon structures in petroleum fractions in the gas-oil region appears to be possible from relationships between the refractive indices and the molecular weights of the different series of pure hydrocarbons. The development of an empirical procedure of ring analysis based only on refractive-index and molecular-weight data is described.

Experimental.

The application of this method of analysis requires the separation of the petroleum fraction into saturated paraffin–naphthene and into aromatic portions. Any suitable procedure of silica-gel extraction which removes all of the unsaturates would be satisfactory, such a method being as follows:

A 125-gram charge of 28- to 200-mesh silica gel, previously heated at 300° to 400° C for 30 hours, is introduced into a 0·65-inch i.d. glass tower and packed to a height of 29 to 30 inches. This gives a height-to-diameter ratio of about 45 to 1. An estimation of the aromatic content of the fraction to be analysed is then made, and a sample of the fraction of such quantity to maintain a ratio of about 25 grams of adsorbent to every gram of aromatic hydrocarbon is introduced at the top of the tower. The adsorptive capacity of the silica gel for aromatics is about 10 per cent of its weight. After the oil has entered the silica gel, *n*-pentane is introduced as a displacing liquid and allowed to filter through the tower. The refractive index of the filtrate is read at intervals, and when it reaches a value of 1·3575, equal to that of the *n*-pentane being used, or shows a sharp increase, a separate receiver is used to collect the aromatic portion. Methanol is then added to desorb the aromatic hydrocarbons, and desorption is considered complete when the refractive index of the filtrate reaches a value equal to that of the methanol being used. The solvents are removed from the products by simple distillation over a steam-bath. Variations in the procedure are permissible if the ratios of height of adsorbent to diameter of tower and weight of adsorbent to weight of aromatics are kept sufficiently high to

insure complete and sharp separation of the aromatics from the naphthene–paraffin portions.

Estimation of Molecular Weight.

The only data required other than the refractive indices at 20° C are the molecular weights of the fractions. These can be determined experimentally, or may be estimated from correlations of certain physical properties with molecular weight. Such a correlation based on the boiling-point and refractive-index data available in the literature [1, 6, 7, 14] on pure hydrocarbons in the kerosine, gas oil, and light neutral range is presented in Fig. 1. This chart relates molecular weight, refractive index, and boiling point by the following expression :—

$$\log_{10} M = 0{\cdot}001098\,(\text{B.P.}) + 1{\cdot}9043 + \log_{10}(2{\cdot}1500 - n_{\text{D}}^{20})$$

A similar system relating molecular weight, boiling point, and density can also be established. In the case of the high-boiling hydrocarbons or petroleum fractions whose boiling points are available only at reduced pressures, conversion to equivalent values at atmospheric pressure may be effected by means of a vapour-pressure chart. The one employed in this work was that constructed by Brown and Badger.[2] Such a procedure may introduce a slight error in the case of aromatics, due to the fact that most vapour-pressure charts are based on the data for paraffins and correlate the data for aromatics only approximately.

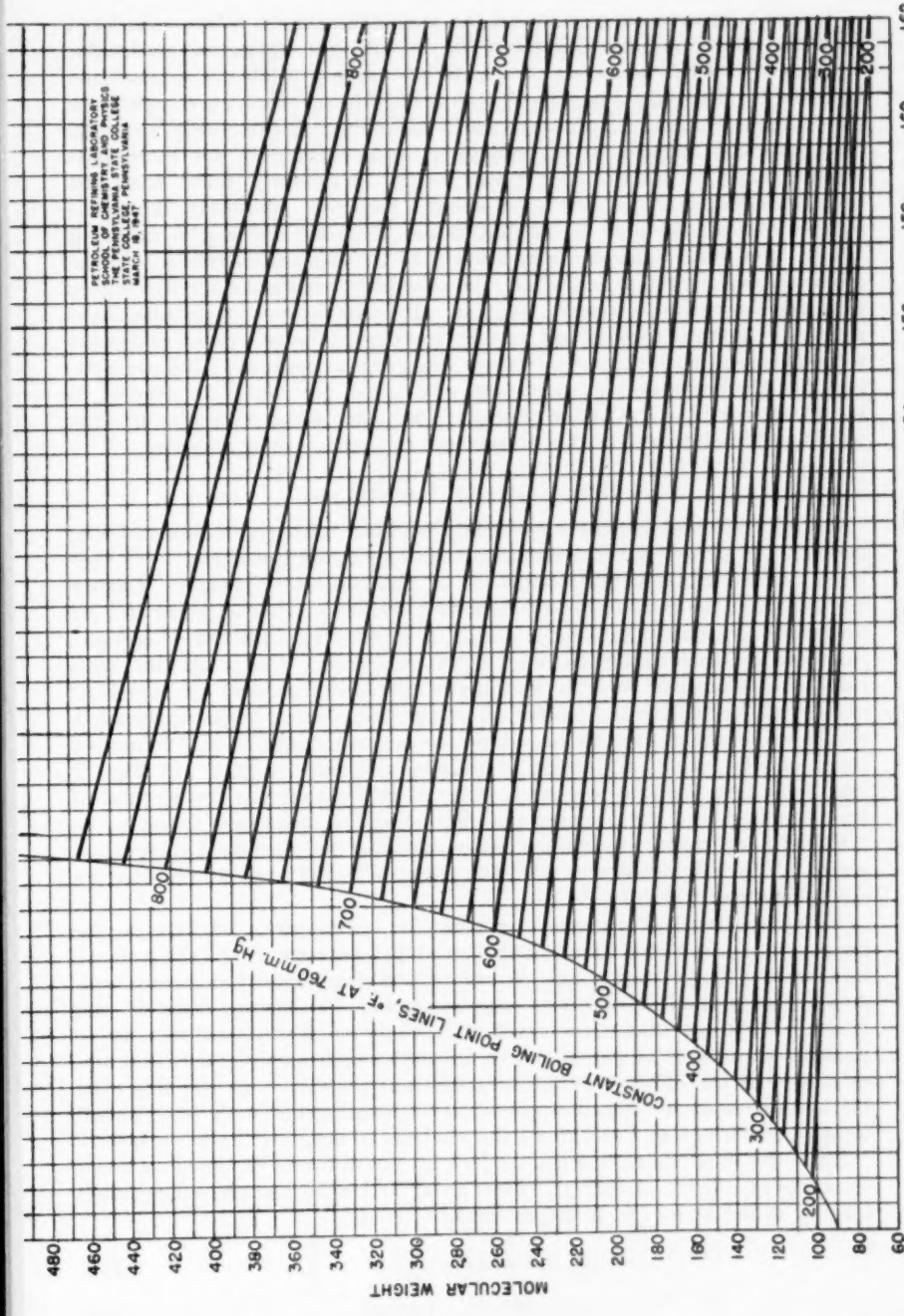
When dealing with narrow-boiling petroleum fractions it is also convenient to assume that the boiling-point ranges of the paraffin–naphthene portion and the aromatic portion separated by silica-gel adsorption are the same and equal to that of the original fraction. This eliminates the necessity of re-determining the boiling points or experimentally measuring the molecular weights of the adsorption fractions. The errors introduced by the above assumptions are not large, as will be noted from the following data comparing calculated and experimental molecular weights of fractions and their portions separated by silica gel :—

Fraction no.	Portion.	50% b.p. at 760 mm, ° F.	Refractive index, n_{D}^{20}.	Molecular weight.	
				Calc.[a]	Experimental.[b]
173	Original	532	1·4640	210	227 [c]
	Paraffin–naphthene . .		1·4519	214	233
	Aromatic (17·5%) . .		1·5307	190	196
209	Original	632	1·4602	273	270 [c]
	Paraffin–naphthene . .		1·4513	277	273
	Aromatic (11·2%) . .		1·5428	240	250
214	Original	648	1·4715	281	279 [c]
	Paraffin–naphthene . .		1·4587	286	284
	Aromatic (16·3%) . .		1·5497	248	254

[a] Calculated from correlation between refractive index, boiling point, and molecular weight (Fig. 1).

[b] Determined by method of Menzies and Wright (*J. Amer. chem. Soc.*, 1921, **43**, 2315).

[c] Estimated from molecular weights and proportions of component portions.


PETROLEUM REFINING LABORATORY
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THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA
MARCH 15, 1947
CONSTANT BOILING POINT LINES, °F. AT 760 m.m. Hg
800
700
600
500
400
300
200
MOLECULAR WEIGHT
480 460 440 420 400 380 360 340 320 300 280 260 240 220 200 180 160 140 120 100 80 60
REFRACTIVE INDEX, n_D^{20}
1.38 1.40 1.42 1.44 1.46 1.48 1.50 1.52 1.54 1.56 1.58 1.60 1.62

Fig. 1.

CORRELATION OF MOLECULAR WEIGHT, REFRACTIVE INDEX, AND BOILING POINT FOR HYDROCARBONS.

A comprehensive comparison of the molecular-weight values calculated from the above equation or from Fig. 1 with the theoretical molecular weights of 688 hydrocarbons on which data were available is summarized in Table I. The results here have been subdivided to show the comparisons for different classes of hydrocarbons in different molecular-weight ranges. The calculated values for all individual hydrocarbons in the molecular-weight range of 100 to 200 appear to be consistently lower than the theoretical values by an average of about 5 per cent. Similarly, the calculated molecular weights of aromatics in the molecular-weight range of 200 to 300 show a tendency to be lower than the theoretical values. In the molecular-weight range below 100, the calculated values are slightly higher than the theoretical molecular weights. In other regions no definite trend is noted. For the total of 688 pure hydrocarbons the calculated molecular weights agreed with the actual values within an average of $\pm$ 5·8 per cent, and the algebraic average deviation was $-$ 4·1 per cent. In general, it would appear that the above procedure for calculating molecular weights would yield values well within 10 per cent of the molecular weights.

Derivation of Equations.

In order to establish the relationship between refractive index and ring content, the refractive-index data available on pure hydrocarbons [1, 6, 7, 11, 14] were plotted against the reciprocal of the molecular weight. Graphs summarizing the relationships found for paraffins and naphthenes and for aromatics are shown in Figs. 2 and 3, respectively. A series of straight lines can be drawn for each homologous series, and it is noted that with increasing molecular weight, and hence increasing number or length of chains, the refractive indices for all of the homologous series approach a single value which can be considered as corresponding to the refractive index of a hypothetical paraffin of infinite molecular weight. In Figs. 2 and 3 the best straight lines were determined by applying the method of least squares, and the limiting paraffin refractive index was found to be 1·4750 by averaging the values determined for the various hydrocarbon series. This is in agreement with the value of 1·4752 recently reported by Smittenberg and Mulder.[15]

By computing the spacings of a point for an unknown mixture on the appropriate graph it is then possible to obtain an estimate of the average number and the average weight per cent of the rings present in the mixture. A similar method of analysis was suggested by Lipkin, Martin, and Kurtz,[9, 10] except that they correlated density coefficient and density to paraffin–naphthene mixtures and to aromatics and density coefficient and refractive index only to paraffin–naphthene mixtures. In the following method a somewhat different approach is made to dispense with the awkward density coefficient and to extend the analysis to aromatic hydrocarbons.

Since the lines shown in Figs. 2 and 3 for the different homologous series converge at infinite molecular weight to $n_D^{20} = 1{\cdot}4750$, the general equation for any of the series can be expressed as follows :—

$$n_D^{20} = 1{\cdot}4750 + \frac{m}{M} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or

$$m = M(n_D^{20} - 1{\cdot}4750) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

Table I.

Deviation of Molecular Weights Calculated by the Boiling-point–Refractive-index Correlation from the Theoretical Values for Pure Hydrocarbons

Molecular-weight range:	<100.			100–200.			200–300.			300–400.			>400.			Total.		
Hydrocarbon type.	No. compounds.	Average deviation, %.	Algebraic average deviation, %.	No. compounds.	Average deviation, %.	Algebraic average deviation, %.	No. compounds.	Average deviation, %.	Algebraic average deviation, %.	No. compounds.	Average deviation, %.	Algebraic average deviation, %.	No. compounds.	Average deviation, %.	Algebraic average deviation, %.	No. compounds.	Average deviation, %.	Algebraic average deviation, %.
Saturated compounds:—																		
Paraffins: normal	2	9·7	+9·7	8	1·5	+1·0	7	2·3	+ 2·3	5	2·6	+2·6	0	—	—	22	2·8	+2·6
branched	5	4·0	+3·6	91	6·0	−6·0	19	8·8	− 8·3	19	4·3	−3·5	12	4·7	−1·5	146	6·0	−5·3
Monocyclopropanes	11	5·6	+3·9	4	6·8	−6·8	0	—	—	0	—	—	0	—	—	15	5·9	+1·0
Monocyclobutanes	6	9·7	+9·7	5	9·3	−9·3	0	—	—	0	—	—	0	—	—	11	9·5	+1·1
Monocyclopentanes	8	3·7	+2·9	40	4·0	−3·6	4	5·4	+ 5·2	4	2·3	+2·3	0	—	—	56	3·9	−1·6
Monocyclohexanes	2	4·6	+4·6	54	4·3	−4·2	26	9·5	− 7·3	16	3·7	+0·5	4	4·3	+3·9	102	5·5	−3·8
Dicyclopentanes	0	—	—	5	4·8	−3·4	0	—	—	2	2·7	+2·5	0	—	—	7	4·2	−1·7
Decalins	0	—	—	16	5·9	−4·9	6	11·7	−11·7	1	0·0	0·0	2	4·7	−2·9	25	7·0	−6·2
Dicyclohexanes	0	—	—	5	3·1	−0·6	3	8·7	− 4·9	5	3·7	−2·8	0	—	—	13	4·6	−2·4
Condensed tricyclics	0	—	—	2	1·8	−0·2	2	6·8	− 6·8	2	5·5	+5·5	0	—	—	6	4·7	−0·5
Tricyclohexanes	0	—	—	0	—	—	4	3·5	− 0·9	2	3·1	+3·1	0	—	—	6	3·4	+0·4
Aromatic compounds:—																		
Benzenes	2	2·4	+2·4	132	6·0	−5·7	40	10·2	− 8·9	21	4·9	+0·1	2	5·2	−3·6	197	6·7	−5·6
Naphthalenes	0	—	—	32	3·2	−2·8	5	6·2	− 4·8	0	—	—	0	—	—	37	3·6	−3·1
Diphenyls	0	—	—	9	3·7	−3·6	21	9·1	− 8·4	4	1·2	+1·2	1	4·7	+4·7	35	6·7	−5·7
Condensed tricyclics	0	—	—	1	5·1	+5·1	1	5·8	− 5·8	1	4·6	+4·6	0	—	—	3	5·2	+1·3
Triphenyls	0	—	—	0	—	—	5	6·6	− 4·8	2	3·1	−3·1	0	—	—	7	5·6	−4·3
Total	36	5·6	+4·9	404	5·2	−4·8	143	8·7	− 7·0	81	3·8	−0·3	21	4·7	−0·5	688	5·8	−4·1

where M is the molecular weight of any particular hydrocarbon of a given series and m is the slope of the line for the given homologous series. The

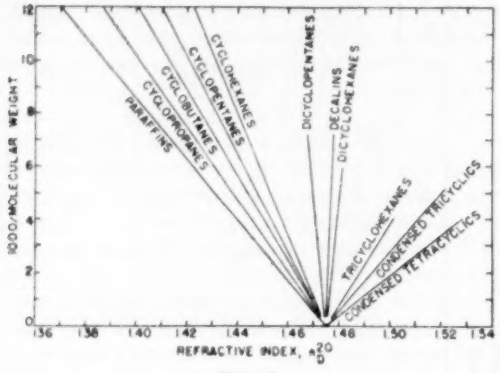


FIG. 2.

RELATION BETWEEN MOLECULAR WEIGHT AND REFRACTIVE INDEX FOR NAPHTHENE AND PARAFFIN HYDROCARBONS.

slopes, m, obtained for the various lines representing the different series are listed in the following table along with the molecular weights of the basic ring structures, M_N or M_A, the number of carbon atoms in ring structure,

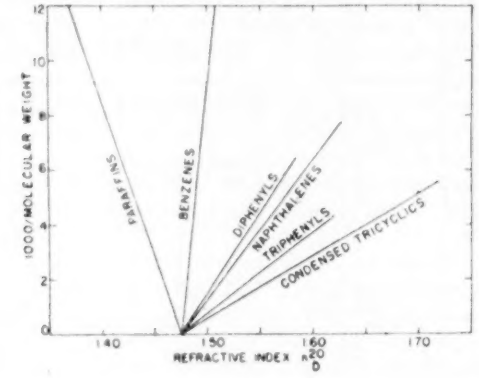


FIG. 3.

RELATION BETWEEN MOLECULAR WEIGHT AND REFRACTIVE INDEX FOR AROMATIC AND PARAFFIN HYDROCARBONS.

C_N or C_A, and the increase in slope over that of the paraffin series, $m + 8{\cdot}79$, caused by the presence of different ring structures is given on page 631.

In the calculation of the molecular weight of the ring portions, M_N or M_A of the hydrocarbons, it was assumed that only one side chain was present per ring. The last column in the above table was computed as the slope of the hydrocarbon series minus that of the paraffin series, so that a differential existed between the paraffin series and other hydrocarbon series

containing ring structures which could subsequently be related to carbon atoms in rings, weight per cent rings, and number of rings, the base line then being the paraffins with no rings present.

Hydrocarbon type.	Carbon atoms in rings, C_N or C_A.	Molecular weight of rings, M_N or M_A.	Slope of refractive index line, m.	Increase in slope over paraffin series $(m + 8{\cdot}79)$.
Saturated compounds (Fig. 2):				
Paraffins	0	0	−8·79	0
Monocyclopropanes	3	41·1	−7·37	1·42
Monocyclobutanes	4	55·1	−6·21	2·58
Monocyclopentanes	5	69·1	−5·41	3·38
Monocyclohexanes	6	83·1	−4·43	4·36
Dicyclopentanes	10	137·2	−1·07	7·72
Decalins	10	137·2	0·32	9·11
Dicyclohexanes	12	165·3	1·00	9·79
Condensed tricyclics	14	191·3	8·94	17·72
Tricyclohexanes	18	247·4	6·56	15·35
Condensed tetracyclics	18	245·4	13·38	22·17
Di-decalins	20	274·5		
Aromatic compounds (Fig. 3):				
Benzenes	6	77·1	2·64	11·42
Naphthalenes	10	127·2	19·5	28·3
Diphenyls	12	153·2	16·8	25·6
Condensed tricyclics	14	177·2	43·6	52·4
Triphenyls	18	229·3	33·2	41·9

Naphthene–Paraffin Mixtures.

For naphthenic compounds, those containing saturated rings with saturated paraffinic side chains, the weight per cent of naphthene rings is calculated by the following method:—

$$\text{Wt-\% naphthene rings} = \frac{M_N}{M}(100) \quad . \quad . \quad . \quad . \quad (2)$$

where M_N is the molecular weight of the basic ring structure and M is the total molecular weight of the compound. It is seen in Fig. 2 and in the

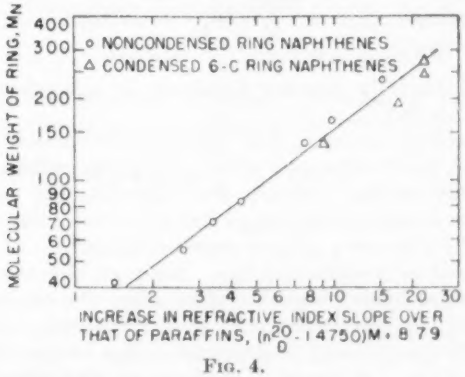


FIG. 4.

RELATIONSHIP OF REFRACTIVE INDEX SLOPE TO RING MOLECULAR WEIGHT FOR NAPHTHENES.

preceding table that the ring molecular weight, M_N, varies with the slope, m, of the refractive index lines or with the increase in slope over that of the paraffin series. The relation between this increase in slope and the molecular weight of the ring portion of the molecules is shown graphically in Fig. 4. If an average line is drawn for the condensed and non-condensed ring naphthenes, the equation expressing the relation is as follows :—

$$M_N = 28{\cdot}9(m + 8{\cdot}79)^{0{\cdot}73} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Combining Equations (1), (2), and (3) yields the following expression for calculating weight per cent of naphthene rings from refractive-index and molecular-weight data :—

$$\text{Average wt-\% naphthene rings} = \frac{2890}{M}[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}73} \quad (4)$$

The above equation gives the portion of the molecules (carbon and hydrogen) occurring as naphthene rings, expressed as a percentage of the total molecular weight, the basis being that the rings and chains are assumed to be saturated, that only one side chain per ring is present, and that the data for monocyclic, dicyclic, and tricyclic naphthenes have been averaged for condensed and non-condensed ring structures. As a matter of interest, a similar equation can be derived for percentage of naphthene rings when the assumption is made that all such rings occur in non-condensed form. This equation is as follows :—

$$\underset{\text{(non-condensed)}}{\text{Wt-\% naphthene rings}} = \frac{2500}{M}[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}83} \quad . \quad (5)$$

Equation (5) for non-condensed naphthene rings differs slightly from Equation (4) for the average of condensed and non-condensed naphthene rings, and may have limited application for mixtures where condensed-ring naphthenes are known to be absent. For mixtures containing only paraffins and condensed six-carbon-atom rings of the type *cyclo*hexane, decalin, perhydro-anthracene, etc., the following specific equation can be developed :—

$$\underset{\text{(condensed)}}{\text{Wt-\% naphthene rings}} = \frac{3280}{M}[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}64} \quad . \quad (5a)$$

It will be noted that the original Equation (4) comprises an average of Equations (5) and (5a).

The error caused by assuming that only one side chain is present per ring can be neglected, since variations within any given series affect the results to a considerably greater extent. For example, the results listed on page 633 are for several *cyclo*hexanes having a molecular weight of 140·3 and on which the refractive indices were available.[6]

1. *Carbon Atoms in Naphthene Rings.* Since an almost equal number of hydrogen atoms are linked to each carbon atom, the expression for calculating the average weight per cent of naphthene rings also gives a close approximation of the per cent of the total carbon atoms which are present as ring carbon atoms. However, a more exact expression can be derived from the relationship shown in Fig. 5, where the number of carbon atoms

Compound.	n_D^{20}.	Theoretical wt-% rings.	Calc. wt-% rings (Eq. 4).
Butyl*cyclo*hexane	1·4410	59·3	57
1-Methyl-2-propyl*cyclo*hexane . . .	1·4445	58·5	60
cis-1 : 2 : 3 : 4-Tetramethyl*cyclo*hexane .	1·4462	57·1	64
trans-1 : 2 : 3 : 4-Tetramethyl*cyclo*hexane .	1·4444	57·1	62
cis-1 : 2 : 4 : 5-Tetramethyl*cyclo*hexane .	1·4442	57·1	62
trans-1 : 2 : 4 : 5-Tetramethyl*cyclo*hexane .	1·4423	57·1	58

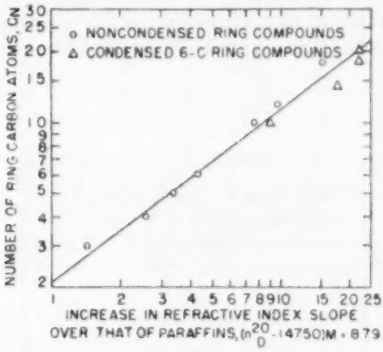

o NONCONDENSED RING COMPOUNDS
Δ CONDENSED 6-C RING COMPOUNDS
NUMBER OF RING CARBON ATOMS, CN
INCREASE IN REFRACTIVE INDEX SLOPE OVER THAT OF PARAFFINS, $(n_D^{20} - 1.4750)M + 8.79$

FIG. 5.

RELATIONSHIP OF REFRACTIVE INDEX SLOPE TO NUMBER OF RING CARBON ATOMS FOR NAPHTHENES.

occurring in ring structure are plotted against the increase in refractive-index slope over that of the paraffins, $m + 8{\cdot}79$, on log-log co-ordinates. The equation for the best straight line averaging the data is as follows :—

$$C_N = 2{\cdot}08(m + 8{\cdot}79)^{0{\cdot}73} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where C_N is the number of carbon atoms in ring structure and m is the slope of the refractive index-molecular weight line in Fig. 2 for a given homologous series. Combining Equations (1) and (6) gives the general equation :—

$$C_N = 2{\cdot}08[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}73} \quad . \quad . \quad . \quad (7)$$

To express the ring structure as the percentage of the total carbon atoms present in rings, the following relation is also employed :—

$$\text{Wt-\% ring carbon} = \frac{C_N}{n}(100) = \frac{1400}{M - x}C_N \quad . \quad . \quad (8)$$

since

$$n = \frac{M - x}{14} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where n is the total average number of carbon atoms per molecule in the mixture and x is the constant in the general formula for hydrocarbons, C_nC_{2n+x}. The value of x for paraffins and naphthenes is given exactly by the following expression :—

$$x = 2(1 - R_N) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where R_N is the average number of naphthene rings per molecule. (A method for estimating this quantity is described below.) Combining Equations (7) to (10), inclusive, yields a general expression for calculating the percentage of ring carbons in paraffin–naphthene mixtures ;—

$$\text{Average wt-\% ring carbon (paraffin–naphthene)} = \frac{2920}{M - 2(1 - R_N)} [(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}73} \quad . \quad (11)$$

The solution of this equation yields the weight percentage of the total carbon atoms occurring in ring structure for the average molecule, the same limitations and assumptions noted above for Equation (4) applying also in this case.

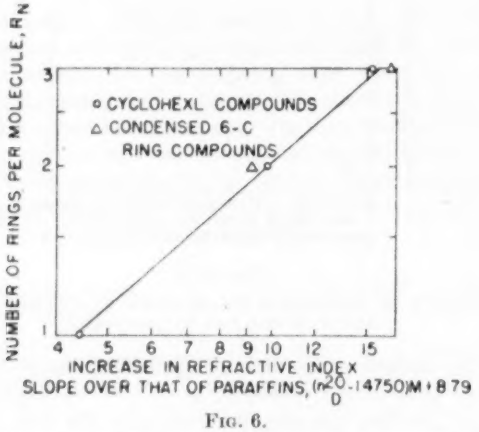


FIG. 6.

RELATIONSHIP OF REFRACTIVE INDEX SLOPE TO NUMBER OF RINGS FOR NAPHTHENES.

2. *Number of Naphthene Rings.* For most practical purposes the correction on the molecular weight for the value of x can be neglected (Eq. (9)), since x varies only from + 2 for paraffins to — 4 for tricyclic naphthenes. The average number of naphthene rings per molecule, however, can be estimated from the relationship between the refractive-index slope and the average number of rings per molecule shown in Fig. 6. This graph is based on the data for pure hydrocarbons having six-membered condensed and non-condensed rings, and the best line through the points can be expressed by the following equation :—

$$\text{Average no. of naphthene rings, } R_N = 0{\cdot}284 [(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}86} \quad . \quad (12)$$

As mentioned previously, the increase in refractive-index slope of the hydrocarbon series over that of the paraffin series was chosen so that the paraffin line would become a reference line for zero rings. The assumption that the rings contain six carbon atoms introduces some error if other sizes of rings are present, the values calculated by Equation (12) decreasing as

the number of carbon atoms per ring decreases. For example, the extent of the deviations can be illustrated by the following data, where the number of naphthene rings is calculated from the average increase in refractive-index–molecular-weight slope, $m + 8{\cdot}79$, for several of the naphthene hydrocarbon series; average data calculated by Equation (12) for various individual members of these series are also shown :—

Hydrocarbons.	Difference in slope, $m + 8{\cdot}79$.	Calc average no. of rings.	No. of compounds examined.	Average of calc values for no. of rings.
*cyclo*Propanes . . .	1·42	0·38	15	0·4
*cyclo*Butanes . . .	2·58	0·64	11	0·6
*cyclo*Pentanes . . .	3·38	0·81	57	0·8
*cyclo*Hexanes . . .	4·36	1·00	108	1·1
Di*cyclo*pentanes . .	7·72	1·65	7	1·6
Di*cyclo*hexanes . .	9·79	2·02	14	2·1

The deviations noted are not considered of primary importance when working in the kerosine and gas-oil range, because of the relatively low chances of encountering appreciable concentrations of *cyclo*propanes and *cyclo*butanes. To date none of these latter structures have been found in any virgin naphtha.

The average number of six-carbon-atom naphthene rings per molecule can also be estimated from the calculated value for the average number of carbon atoms occurring in ring structure, C_N. For the average of six-carbon-atom condensed and non-condensed rings, the following approximate relation exists :—

$$C_N = 5R_N + 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Combining this with Equation (7) yields the following expression :—

$$R_N = 0{\cdot}417[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}73} - 0{\cdot}2 \quad . \quad . \quad (14)$$

The calculated values obtained by Equation (14) are in fair agreement with those given by Equation (12) for the range of naphthene hydrocarbons investigated. However, when paraffins are present in high concentrations or when applied to naphthenes in the high-molecular-weight range the results diverge, as may be noted from the following comparisons :—

Assumed value of $(m + 8{\cdot}79)$.	Average no. of rings per molecule.		Deviation, %.
	Calc by Eq. (12).	Calc by Eq. (14).	
−8·79	0	−0·20	—
4·3	0·99	1·01	2
9·5	1·95	1·96	1
16	3·06	2·97	3
22	4·02	3·80	5
30	5·25	4·82	8

No reliable data are available on pure polycyclic naphthenes of four and five rings, and since the correlations are empirical, the form derived from

experimental data; namely, Equation (12), is preferred for calculating average number of naphthene rings per molecule.

For the correction term on the molecular weight included in Equation (11) for calculating the average weight per cent of carbon atoms in ring structure, either Equation (12) or (14) may be used, the complete equation then taking the following forms :—

$$\text{Average wt-\% ring carbon (paraffin–naphthene)} = \frac{2920[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}73}}{M - 2 + 0{\cdot}57[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}86}} \quad . \quad (15)$$

$$\text{Average wt-\% ring carbon (paraffin–naphthene)} = \frac{2920[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}73}}{M - 2{\cdot}4 + 0{\cdot}834[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}73}} \quad . \quad (16)$$

A comparison of the results that would be obtained by the above equations for similar values of $(m + 8{\cdot}79)$ and M are indicated in the following table, together with the results that would be obtained if no correction term is employed :—

Class of naphthenes.	Assumed values.		Calc wt-% ring carbon.		
	$(m + 8{\cdot}79)$.	M.	Eq. (15).	Eq. (16).	Eqs. (7) and (8) $x = 0$.
Monocyclics . .	4·3	100	84·7	84·7	84·4
		200	42·3	42·3	42·2
Dicyclics . .	9·5	200	75·0	75·0	75·5
		300	50·0	50·0	50·2
Tricyclics . .	16	300	72·7	72·8	73·6
		400	54·7	54·8	55·2
Tetracyclics . .	22	350	78·4	78·5	79·5
		500	55·0	55·1	55·6

As will be noted the calculated values are essentially the same in all cases, and even when no correction term is used (last column) the divergence is well within experimental precision. Equation (15) is preferred for the same reasons mentioned above; however, Equation (16) is more convenient to use.

Summarizing the methods of analysis of paraffin–naphthene mixtures, it will be noted that equations are derived for calculating the following items : (Eq. (4)) average weight per cent of naphthene rings, (Eq. (7)) average number of carbon atoms in ring structure, (Eq. (11) or (15)) average weight per cent of the total carbon atoms per molecule occurring in ring structure, and (Eq. (12)) the average number of six-carbon-atom rings per molecule. To facilitate solution of these equations, several nomographs have been constructed and are shown in Figs. 7 and 8. Fig. 7 is a nomograph for estimating the average number of rings per molecule (Eq. (12)) and the

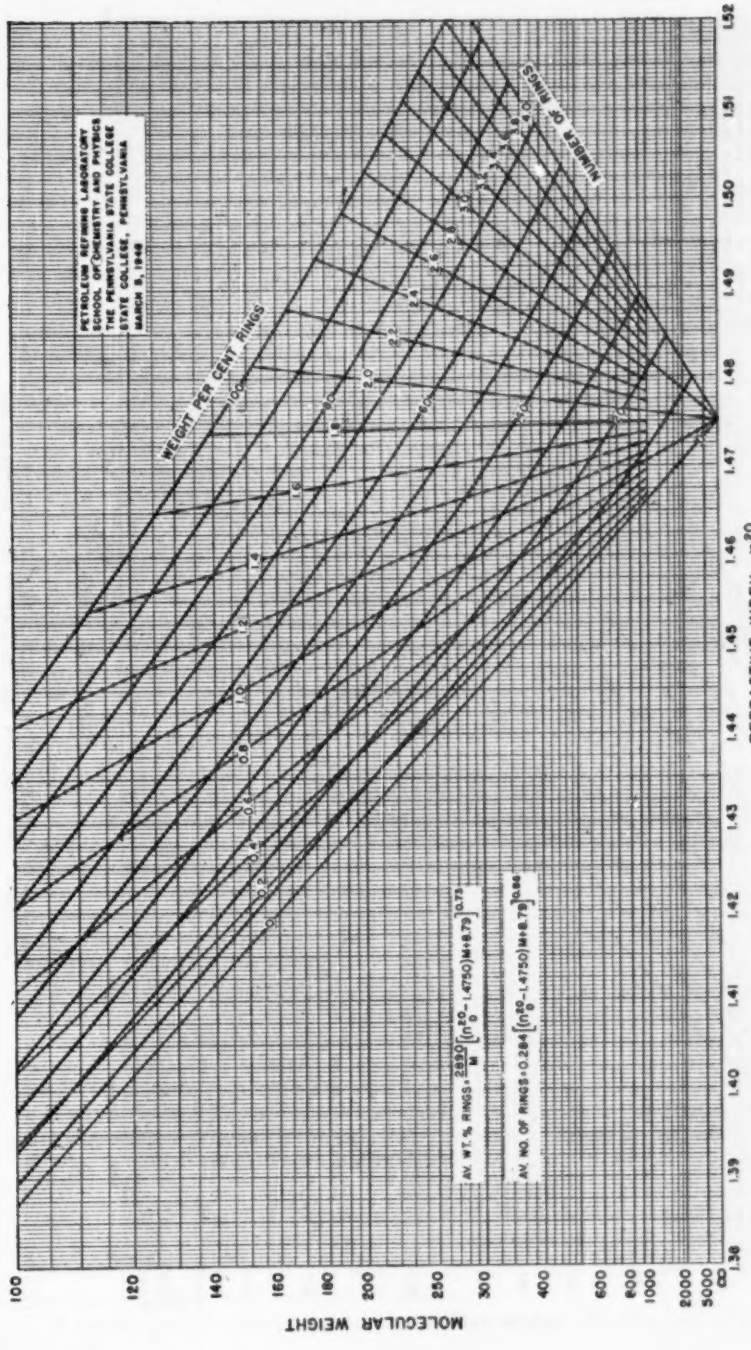

PETROLEUM REFINING LABORATORY
SCHOOL OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA
MARCH 5, 1948
WEIGHT PER CENT RINGS
NUMBER OF RINGS
AV. WT. % RINGS = 2820/M (n_D^20 − 1.4750)M+0.79)^0.75
AV. NO. OF RINGS = 0.284 ((n_D^20 − 1.4750)M+0.79)^1.65
MOLECULAR WEIGHT
REFRACTIVE INDEX, n_D^20

FIG. 7.

AVERAGE NUMBER OF RINGS PER MOLECULE AND WEIGHT PER CENT RINGS FOR MIXTURES OF PARAFFINS AND NAPHTHENES.

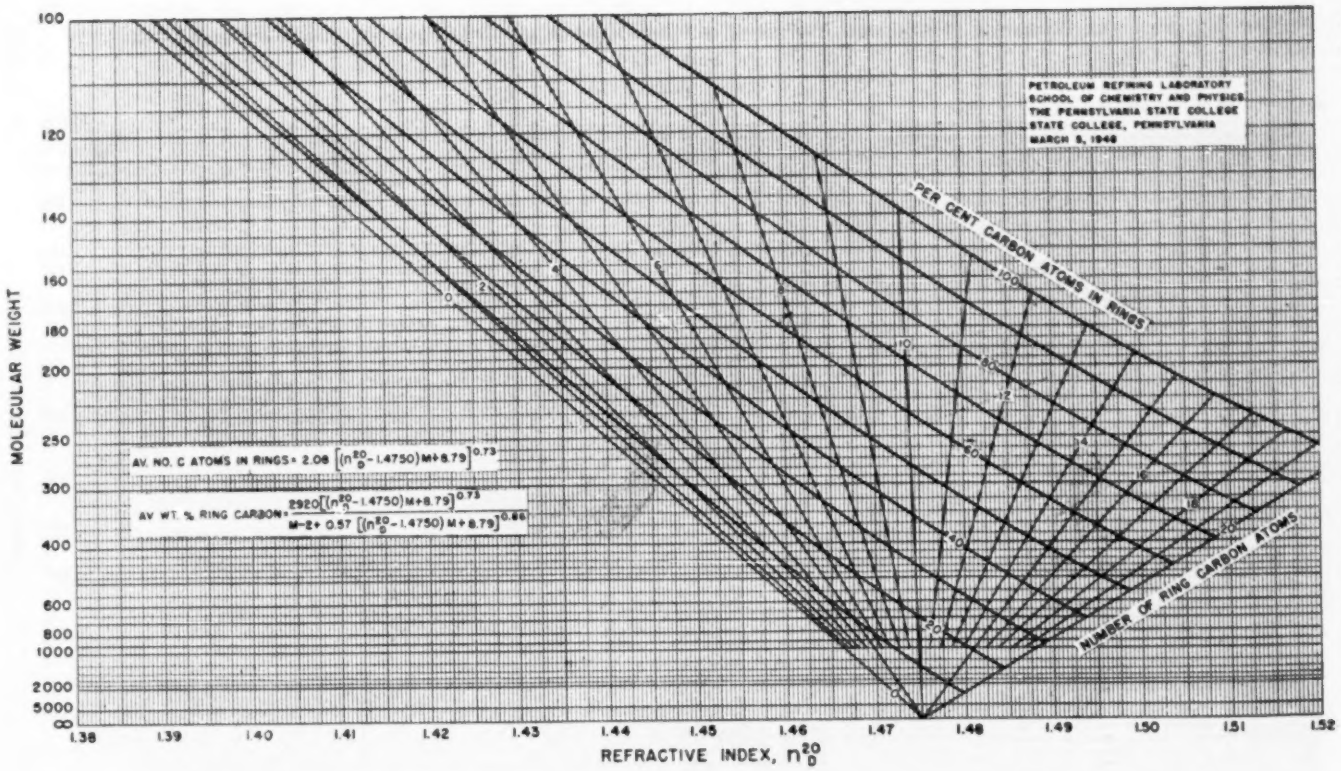


FIG. 8.

AVERAGE NUMBER OF RING CARBON ATOMS PER MOLECULE AND PER CENT OF TOTAL CARBON ATOMS PRESENT AS RINGS FOR MIXTURES FOR PARAFFINS AND NAPHTHENES.

average weight per cent naphthene rings (Eq. (4)). In using the chart the point located by the given refractive index and molecular weight of the compound or mixture also permits the estimation of number of rings and weight per cent rings from the scales superimposed on the chart. For example, if the molecular weight and refractive index of an unknown are given as 154 and 1·4500, respectively, the point located by these co-ordinates is seen to fall on the line indicated as 60 weight per cent naphthene rings and about midway between the lines marked 1·0 and 1·2 rings per molecule, or the average number of rings per molecule is 1·1. Fig. 8 is a nomograph for estimating the average number of carbon atoms occurring in ring structure (Eq. (7)) and the weight per cent of the total carbon atoms in rings (Eq. (15)). The procedure for use of this chart is the same as that described for Fig. 7.

In general, the methods developed above are applicable with a reasonable degree of accuracy to mixtures of saturated hydrocarbons of the type used for establishing the basic relations. While the precision of the analytical methods will be discussed in greater detail later, it should be pointed out that the values obtained by the above equations are concerned only with the ring portions, and the values obtained by these methods are probably not sufficiently accurate to draw any definite conclusions regarding the nature and extent of the portions not included in the rings. For example, in mixtures of paraffins and monocyclic and dicyclic naphthenes with six-carbon-atom rings and approximately equal molecular weights, the proportions of condensed rings (decalins) are given by the following equations:—

$$\text{Wt-\% decalins} = 300\ (\text{no. of rings}) - 50\ (\text{no. C atoms in rings}) \quad (17)$$

Variations in the experimental data and calculated values, however, preclude the application of the derived data to such a sensitive procedure, as will be noted from the data given below for some decalin derivatives :—

Compound.	Refractive index, n_D^{20}.	Calc no. of rings, R_N.	Calc no. of C atoms in rings, C_N.	Calc wt-% decalins, $(3R_N - C_N/2)100$.
cis-Decalin . . .	1·4811(6)	2·0	11·0	50
trans-Decalin . .	1·4697(6)	1·7	9·5	35
2-Ethyldecalin . .	1·4776(7)	1·9	10·5	45
3-Ethyldecalin . .	1·4719(7)	1·7	9·8	20
cis-1 : 5-Dimethyldecalin	1·4814(7)	2·0	10·8	60
Propyldecalin . .	1·4776(6)	1·9	10·6	40

Aromatic Mixtures.

Equations similar to those for paraffin–naphthene mixtures can be derived for mixtures of aromatics and paraffins, based on the data given in Fig. 3. The relation between the molecular weight of the aromatic ring portion, M_A, and the differences in slope of the refractive-index–molecular-weight lines for aromatic and paraffin hydrocarbons ($m + 8{\cdot}79$) is shown in Fig. 9. It will be noted that the points for condensed- and non-condensed-ring aromatics fall on separate straight lines, but that an average line for all of the data can also be drawn.

A similar graph correlating the quantity ($m + 8{\cdot}79$) with the number of

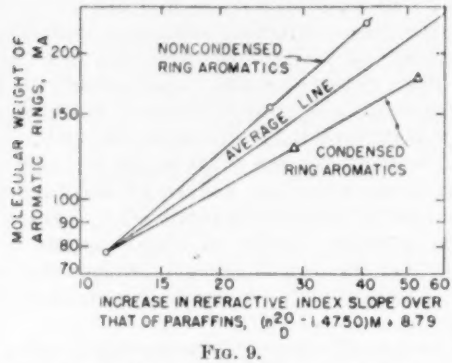


FIG. 9.

RELATIONSHIP OF REFRACTIVE INDEX SLOPE TO RING MOLECULAR WEIGHT FOR AROMATICS.

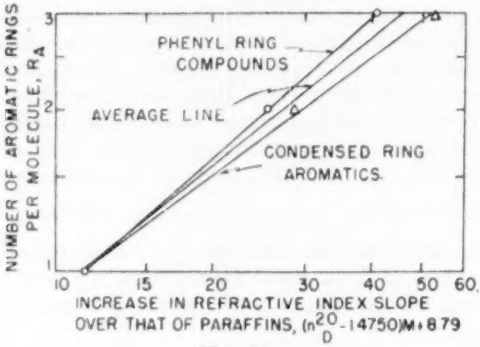

NUMBER OF AROMATIC RINGS PER MOLECULE, R_A
3
2
1
PHENYL RING COMPOUNDS
AVERAGE LINE
CONDENSED RING AROMATICS
10 15 20 30 40 50 60
INCREASE IN REFRACTIVE INDEX SLOPE OVER THAT OF PARAFFINS, $(n_D^{20} - 1.4750)M + 8.79$

FIG. 10.

RELATIONSHIP OF REFRACTIVE INDEX SLOPE TO NUMBER OF RINGS FOR AROMATICS.

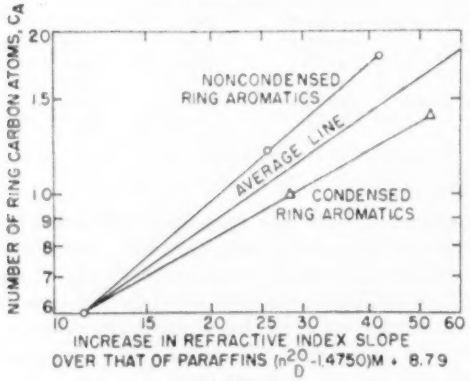


FIG. 11.

RELATIONSHIP OF REFRACTIVE INDEX SLOPE TO NUMBER OF RING CARBON ATOMS FOR AROMATICS.

aromatic rings per molecule, R_A, is also shown in Fig. 10. In this plot data for condensed- and non-condensed-ring aromatics diverge from the average for polycyclic aromatics.

Fig. 11 shows the relationship between the number of carbon atoms occurring in six-membered aromatic rings, C_A, and the increase in the refractive-index slope over that of paraffins, $m + 8{\cdot}79$. Again, different curves are required for correlating the data for condensed- and non-condensed-ring aromatics.

A consideration of the correlations given in Figs. 9, 10, and 11 indicates that separate procedures of analysis might be employed for the following cases: (1) mixtures containing only non-condensed-ring aromatics, (2) mixtures containing only condensed-ring aromatics, and (3) unknown mixtures, where an approximation of the ring analysis can be obtained from the use of the average correlations. The latter procedure would probably not introduce serious errors except in the high-molecular-weight range, where the curves for condensed- and non-condensed-ring aromatics diverge to a greater extent. This divergence is due to the fact that for the same molecular weight and the same number of rings per molecule the condensed-ring aromatics have higher refractive indices than the corresponding non-condensed-ring aromatics, as may be seen by reference to Fig. 3. The use of density instead of refractive index may provide slightly better correlation of the data, but individual variations would again be large, and accurate densities are more difficult to obtain experimentally than refractive indices.

To complete the discussion of the ring analysis of aromatic mixtures, the derivations of equations for the three procedures outlined above are briefly discussed in the following sections.

1. *Non-condensed-ring Aromatics.* For mixtures containing only non-condensed-ring aromatics; that is, phenyl alkanes, diphenyl alkanes, triphenyl alkanes, etc., the basic equations for the corresponding curves in Figs. 9, 10, and 11 are as follows:—

$$M_A = 9{\cdot}92\ (m + 8{\cdot}79)^{0{\cdot}84} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

$$R_A = 0{\cdot}126\ (m + 8{\cdot}79)^{0{\cdot}85} \quad . \quad . \quad . \quad . \quad (19)$$

$$C_A = 0{\cdot}758\ (m + 8{\cdot}79)^{0{\cdot}85} \quad . \quad . \quad . \quad . \quad (20)$$

The general equations for calculating the weight per cent of aromatic rings and the weight per cent of ring carbon (per cent of total carbon atoms occurring in phenyl rings) are as follows:—

$$\text{Wt-}\% \text{ aromatic rings} = \frac{M_A}{M}\,(100) \quad . \quad . \quad . \quad . \quad (21)$$

$$\text{Wt-}\% \text{ ring carbon} = \frac{C_A}{n}\,(100) \quad . \quad . \quad . \quad . \quad (22)$$

where n is the total number of carbon atoms per molecule in the general formula, C_nH_{2n+x}; that is,

$$n = \frac{M - x}{14} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

In the case of non-condensed-ring aromatics, the value of x is given by the following relation :—

$$x = 2 - \frac{4}{3} C_A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

or since $C_A = 6R_A$,

$$x = 2 - 8R_A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Using combinations of Equations (1), (9), and (18) to (24), inclusive, the following expressions are obtained :—

$$\text{Wt-\% aromatic rings (non-condensed)} = \frac{992}{M} [(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}84} \quad . \quad . \quad (25)$$

$$\text{No. of aromatic rings, } R_A \text{ (non-condensed)} = 0{\cdot}126[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}85} \quad . \quad (26)$$

$$\text{No. of ring carbons, } C_A \text{ (non-condensed)} = 0{\cdot}758\,[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}85} \quad . \quad (27)$$

$$\text{Wt-\% ring carbon (non-condensed)} = \frac{1060[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}85}}{M - 2 + 1{\cdot}01[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}85}} \quad (28)$$

2. *Condensed-ring Aromatics.* For mixtures containing condensed-ring aromatics, including alkyl benzenes, alkyl naphthalenes, alkyl anthracenes or phenanthrenes, etc., the basic equations for the curves shown in Figs. 9, 10, and 11 are as follows :—

$$M_A = 20{\cdot}2\ (m + 8{\cdot}79)^{0{\cdot}55} \quad . \quad . \quad . \quad . \quad (29)$$

$$R_A = 0{\cdot}165\ (m + 8{\cdot}79)^{0{\cdot}74} \quad . \quad . \quad . \quad . \quad (30)$$

$$C_A = 1{\cdot}54\ (m + 8{\cdot}79)^{0{\cdot}56} \quad . \quad . \quad . \quad . \quad (31)$$

The value of x in the general formula C_nH_{2n+x} for condensed-ring aromatic hydrocarbons is given by either of the following equations :—

$$x = -6R_A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

$$x = 3 - 1{\cdot}5C_A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

Both of these equations give the correct answer for mixtures of condensed-ring aromatics, but the latter equation is probably more suitable if paraffins are also present in the mixture. This can be illustrated by the following data for mixtures of condensed-ring aromatics and paraffins of about the same molecular weight :—

Mixture no.	Wt-% of hydrocarbons present.	Theoretical.			Calc x.	
		R_A.	C_A.	x.	Eq. 32.	Eq. 33.
1	40% amylbenzene 60% methylnaphthalene	1·6	8·4	−9·6	−9·6	−9·6
2	40% amylbenzene 40% methylnaphthalene 20% undecane	1·2	6·4	−6·8	−7·2	−6·6
3	10% amylbenzene 10% methylnaphthalene 80% undecane	0·2	1·6	−0·2	−1·2	+0·6

In aromatic mixtures separated by silica-gel adsorption or other suitable methods no paraffins as such should be present.

Complete equations for the ring analysis of condensed-ring aromatics, similar to those derived for the non-condensed-ring aromatics are given as follows :—

$$\text{Wt-\% aromatic rings (condensed)} = \frac{2020}{M}[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}55} \quad . \quad . \quad (34)$$

$$\text{No. of aromatic rings, } R_A \text{ (condensed)} = 0{\cdot}165[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}74} \quad . \quad (35)$$

$$\text{No. of ring carbons, } C_A \text{ (condensed)} = 1{\cdot}54[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}56} \quad . \quad (36)$$

$$\text{Wt-\% ring carbon (condensed)} = \frac{2150[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}56}}{M + 0{\cdot}99[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}74}} \quad . \quad (37)$$

$$= \frac{2150[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}56}}{M - 3 + 2{\cdot}3[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}56}} \quad (38)$$

3. *Mixtures of Condensed- and Non-condensed-ring Aromatics.* In unknown mixtures of aromatics or in mixtures where both condensed- and non-condensed-ring-type aromatic hydrocarbons are equally apt to be present, the estimation of the ring analysis may be computed more plausibly from the average relations for all types of aromatics. The equations for the average lines indicated in Figs. 9, 10, and 11 are given as follows, some weighting of the points having been executed on the basis of the amount of experimental data available :—

$$M_A = 15{\cdot}5\ (m + 8{\cdot}79)^{0{\cdot}66} \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

$$R_A = 0{\cdot}151\ (m + 8{\cdot}79)^{0{\cdot}78} \quad . \quad . \quad . \quad . \quad . \quad (40)$$

$$C_A = 1{\cdot}18\ (m + 8{\cdot}79)^{0{\cdot}67} \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

For mixtures of all types of aromatics the value of x in the general formula can be obtained by the following relation :—

$$x = 2 - 1{\cdot}4C_A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

Using proper combinations of Equations (1), (9), (21), (22), (39), (40), (41), and (42), therefore, the following expressions for the ring analysis of aromatic mixtures can be derived :—

$$\text{Average wt-\% aromatic rings} = \frac{1550}{M}[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}66} \quad . \quad (43)$$

$$\text{Average no. of aromatic rings, } R_A = 0{\cdot}151[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}78} \quad . \quad (44)$$

$$\text{Average no. of ring carbons, } C_A = 1{\cdot}18[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}67} \quad . \quad (45)$$

$$\text{Average wt-\% ring carbon} = \frac{1650[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}67}}{M - 2 + 1{\cdot}65[(n_D^{20} - 1{\cdot}4750)M + 8{\cdot}79]^{0{\cdot}67}} \quad . \quad (46)$$

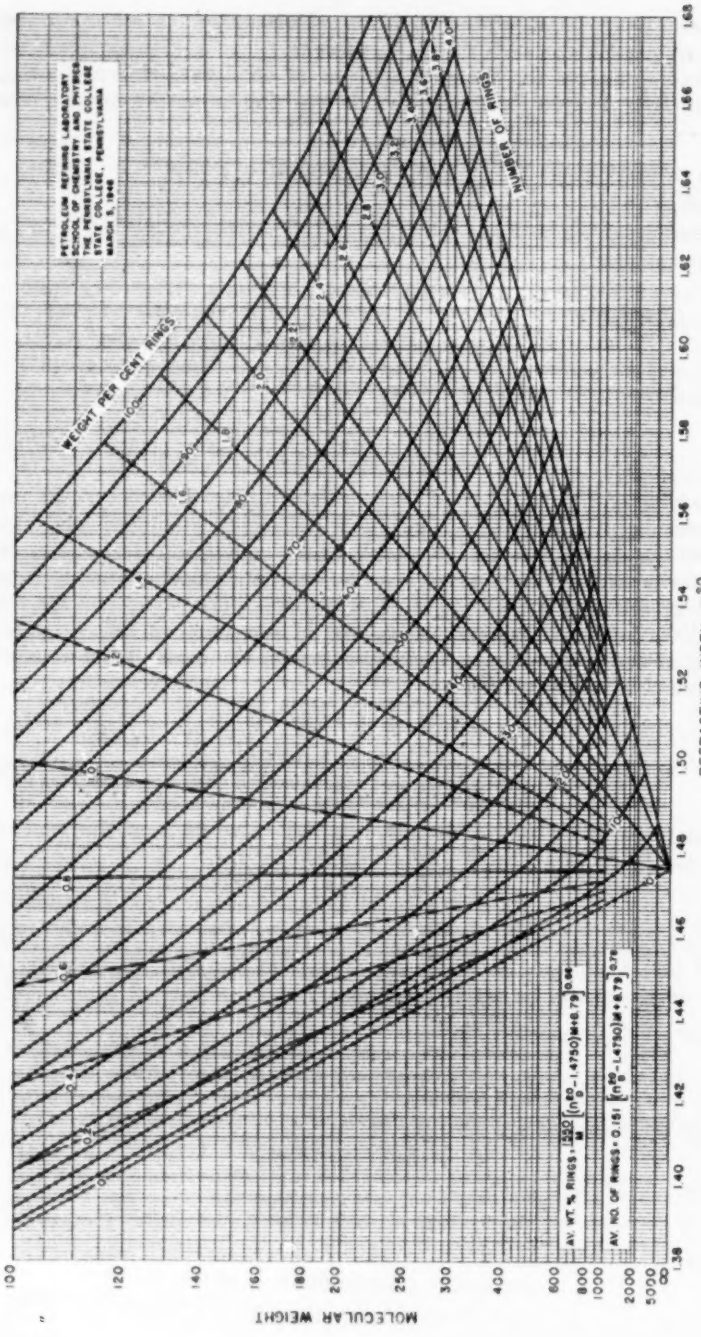


FIG. 12.

AVERAGE NUMBER OF RINGS PER MOLECULE AND WEIGHT PER CENT RINGS FOR MIXTURES OF PARAFFINS AND AROMATICS.

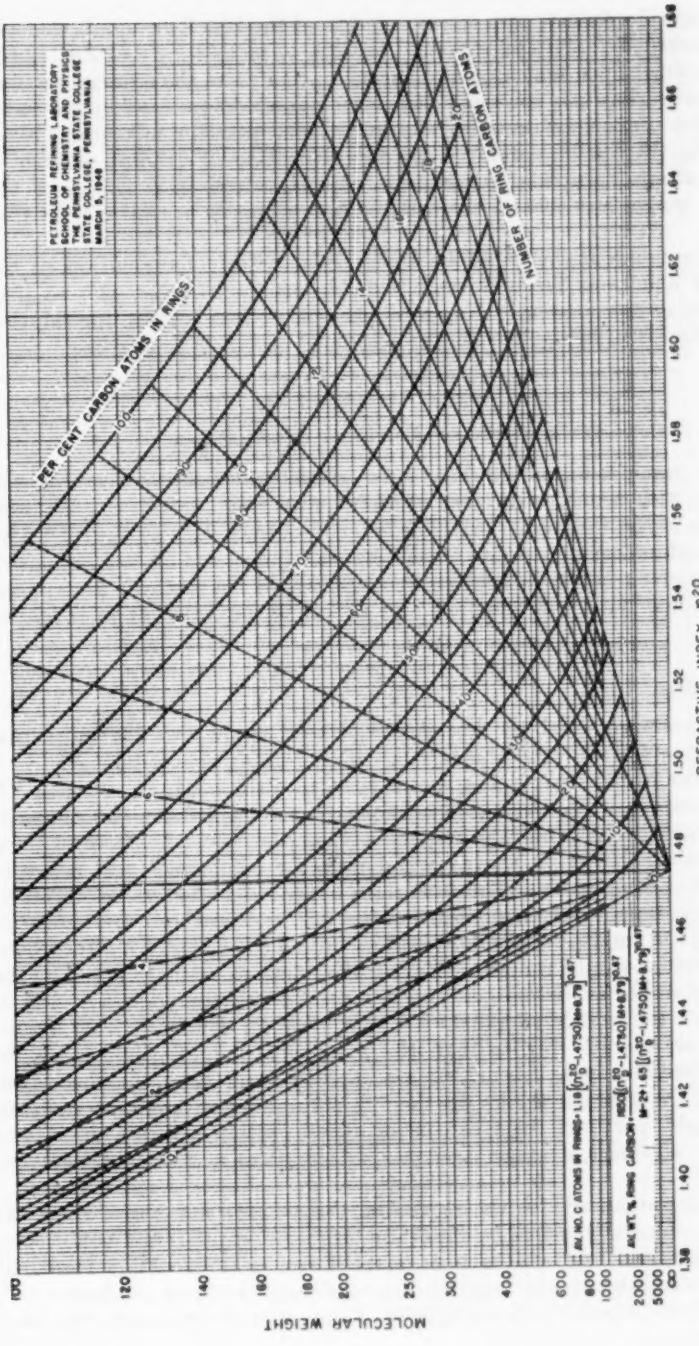


Fig. 13.

AVERAGE NUMBER OF RING CARBON ATOMS PER MOLECULE AND PER CENT OF TOTAL CARBON ATOMS PRESENT AS RINGS FOR MIXTURES OF PARAFFINS AND AROMATICS.

Nomographs for the convenient solution of the last four equations have been constructed, and are presented in Figs. 12 and 13. From Fig. 12 the average weight per cent aromatic rings (Eq. (43)) and the average number of aromatic rings per molecule (Eq. (44)) can be determined by the same procedure previously described for naphthene–paraffin mixtures. Similarly, Fig. 13 can be employed for the estimation of average number of carbon atoms occurring in aromatic ring structure (Eq. (45)) and the average weight per cent of the total carbon atoms in aromatic rings (Eq. (46)).

Similar nomographs could be constructed readily for solution of the series of equations for non-condensed-ring aromatics (Eqs. (25) to (28), inclusive) or for condensed-ring aromatics (Eqs. (34) to (38), inclusive) if the method is to be applied only to restricted classes of aromatics.

Application of Methods of Analysis.

While some information has been given previously concerning the accuracy with which predictions of the average ring analysis can be made by means of the equations derived from experimental data on the refractive indices and molecular weights of pure hydrocarbons, a more comprehensive survey is given in the following discussion where the methods are applied to individual pure hydrocarbons and to known mixtures of pure hydrocarbons.

Pure Hydrocarbons.

The method of analysis described has been applied to 722 individual hydrocarbons on which reliable refractive-index data were available.[1, 6, 7, 11, 14] The results of this survey are summarized in Tables III, IV, V, and VI. For estimation of the average weight per cent of naphthene and aromatic rings, Equations (4) and (43), respectively, were employed. Both of these equations are based on the averaged data for condensed- and non-condensed-ring compounds. The deviations of the calculated values from the theoretical weight per cent rings for the 722 hydrocarbons are shown in Table II, the results being subdivided according to classes of hydrocarbons and molecular-weight ranges. Because the relations used are based on the average data for condensed- and non-condensed-ring compounds, it will be noted that the calculated weight per cent rings for condensed-ring hydrocarbons are slightly higher than the theoretical values, while those for non-condensed-ring hydrocarbons are slightly lower than the theoretical values. The average results for the 722 hydrocarbons, however, indicate that weight per cent rings can be estimated within about 7 units, and that the algebraic average deviation is less than + 2 weight per cent rings.

A similar summary for the results on the average number of rings per molecule, calculated either by Equation (12) with paraffins and naphthenes or by Equation (44) with aromatics, is shown in Table III. Here the effect of using the average relations for condensed- and non-condensed-ring hydrocarbons is practically negligible. As mentioned previously, the basic

TABLE II.

Difference between Calculated and Theoretical Weight per cent Rings for Pure Hydrocarbons.

Molecular-weight range:	<100.			100–200.			200–300.			300–400.			>400.			Total.		
Hydrocarbon type.	No. compounds.	Average deviation, wt-% rings.	Algebraic average deviation, wt-% rings.	No. compounds.	Average deviation, wt-% rings.	Algebraic average deviation, wt-% rings.	No. compounds.	Average deviation, wt-% rings.	Algebraic average deviation, wt-% rings.	No. compounds.	Average deviation, wt-% rings.	Algebraic average deviation, wt-% rings.	No. compounds.	Average deviation, wt-% rings.	Algebraic average deviation, wt-% rings.	No. compounds.	Average deviation, wt-% rings.	Algebraic average deviation, wt-% rings.
Saturated compounds:—																		
Paraffins: normal	2	12	+12	8	6	− 5	7	6	− 6	5	5	− 5	0	—	—	22	6	− 4
branched	5	10	+ 1	91	13	+ 3	20	7	− 1	20	4	− 3	12	4	−1	148	10	+ 1
Monocyclopropanes	11	10	0	4	12	−10	0	—	—	0	—	—	0	—	—	15	11	− 2
Monocyclobutanes	6	3	+ 2	5	8	− 1	0	—	—	0	—	—	0	—	—	11	5	0
Monocyclopentanes	8	8	− 3	40	7	− 2	4	1	+ 1	5	1	+ 1	0	—	—	57	6	+ 2
Monocyclohexanes	2	8	− 2	58	8	+ 1	26	7	+ 6	17	1	0	4	2	+2	107	7	+ 2
Dicyclopentanes	0	—	—	5	7	− 5	0	—	—	2	5	− 5	0	—	—	7	6	− 5
Decalins	0	—	—	16	8	+ 3	7	8	+ 6	2	5	+ 5	3	4	+4	28	7	+ 4
Dicyclohexanes	0	—	—	5	10	− 6	3	8	− 2	6	5	− 4	0	—	—	14	7	− 4
Condensed tricyclics	0	—	—	2	16	+16	2	23	+23	2	4	+ 4	0	—	—	6	14	+14
Tricyclohexanes	0	—	—	0	—	—	4	13	−13	2	12	−12	0	—	—	6	13	−13
Aromatic compounds:—																		
Benzenes	2	3	− 3	132	4	+ 3	41	3	+ 2	22	1	0	2	1	0	199	3	+ 2
Naphthalenes	0	—	—	32	11	+11	9	7	+ 7	3	4	+ 4	5	3	+3	49	9	+ 9
Diphenyls	0	—	—	9	9	− 9	21	9	− 9	5	7	− 7	3	6	−6	38	8	− 8
Condensed tricyclics	0	—	—	3	19	+19	3	19	+19	1	10	+10	0	—	—	7	18	+18
Triphenyls	0	—	—	0	—	—	5	16	−16	3	15	−15	0	—	—	8	16	−16
Total	36	8	0	410	8	+ 2	152	7	0	95	4	− 2	29	4	0	722	7	+ 1·5

TABLE III.

Difference between Calculated and Theoretical Number of Rings per Molecule for Pure Hydrocarbons.

Molecular-weight range :	<100.			100–200.			200–300.			300–400.			>400.			Total.		
Hydrocarbon type.	No. compounds.	Average deviation, no. rings.	Algebraic average deviation, no. rings.	No. compounds.	Average deviation, no. rings.	Algebraic average deviation, no. rings.	No. compounds.	Average deviation, no. rings.	Algebraic average deviation, no. rings.	No compounds.	Average deviation, no. rings.	Algebraic average deviation, no. rings.	No. compounds.	Average deviation, no. rings.	Algebraic average deviation, no. rings.	No. compounds.	Average deviation, no. rings.	Algebraic average deviation, no. rings.
Saturated compounds :—																		
Paraffins : normal	2	0·1	+0·1	8	0·1	−0·1	7	0·1	−0·1	5	0·2	−0·2	0	—	—	22	0·1	−0·1
branched	5	0·1	0·0	91	0·2	0·0	20	0·2	0·0	20	0·1	−0·1	12	0·2	−0·1	148	0·2	0·0
Monocyclopropanes	11	0·6	−0·6	4	0·7	−0·7	0	—	—	0	—	—	0	—	—	15	0·6	−0·6
Monocyclobutanes	6	0·4	−0·4	5	0·4	−0·4	0	—	—	0	—	—	0	—	—	11	0·4	−0·4
Monocyclopentanes	8	0·3	−0·3	40	0·3	−0·3	4	0·2	−0·2	5	0·2	−0·2	0	—	—	57	0·2	−0·2
Monocyclohexanes	2	0·1	0·0	58	0·2	0·0	26	0·3	+0·2	17	0·1	0·0	4	0·2	+0·2	107	0·2	+0·1
Dicyclopentanes	0	—	—	5	0·3	−0·3	0	—	—	2	0·4	−0·4	0	—	—	7	0·4	−0·4
Decalins	0	—	—	16	0·2	−0·1	7	0·2	0·0	2	0·2	0·0	3	0·1	+0·1	28	0·2	−0·1
Dicyclohexanes	0	—	—	5	0·2	+0·1	3	0·3	+0·1	6	0·2	+0·1	0	—	—	14	0·2	+0·1
Condensed tricyclics	0	—	—	2	0·4	+0·1	2	0·6	+0·6	2	0·2	−0·2	0	—	—	6	0·4	+0·2
Tricyclohexanes	0	—	—	0	—	—	4	0·2	0·0	2	0·1	−0·1	0	—	—	6	0·2	−0·1
Aromatic compounds :—																		
Benzenes	2	0·0	0·0	152	0·1	0·0	41	0·1	+0·1	22	0·1	0·0	2	0·0	0·0	199	0·1	0·0
Naphthalenes	0	—	—	32	0·1	+0·1	9	0·1	0·0	3	0·0	0·0	5	0·1	0·0	49	0·1	+0·1
Diphenyls	0	—	—	9	0·1	0·0	21	0·1	−0·1	5	0·2	−0·2	3	0·2	−0·2	38	0·1	−0·1
Condensed tricyclics	0	—	—	3	0·3	+0·3	3	0·4	+0·4	1	0·3	+0·3	0	—	—	7	0·3	+0·3
Triphenyls	0	—	—	0	—	—	5	0·2	−·2	3	0·3	−0·3	0	—	—	8	0·2	−0·2
Total :																		
Overall	36	0·3	−0·2	410	0·1	0·0	152	0·2	0·0	95	0·1	−0·1	29	0·2	0·0	722	0·16	−0·03
Excluding other rings than six-membered	11	0·1	0·0	356	0·1	0·0	148	0·2	0·0	88	0·1	−0·1	29	0·2	0·0	632	0·13	+0·02

TABLE IV.

Difference between Calculated and Theoretical Number of Ring Carbon Atoms per Molecule for Pure Hydrocarbons.

Molecular-weight range:	<100.			100–200.			200–300.			300–400.			>400.			Total.		
Hydrocarbon type.	No. compounds.	Average deviation, ring carbons.	Algebraic average deviation, ring carbons.	No. compounds.	Average deviation, ring carbons.	Algebraic average deviation, ring carbons.	No. compounds.	Average deviation, ring carbons.	Algebraic average deviation, ring carbons.	No. compounds.	Average deviation, ring carbons.	Algebraic average deviation, ring carbons.	No. compounds.	Average deviation, ring carbons.	Algebraic average deviation, ring carbons.	No. compounds.	Average deviation, ring carbons.	Algebraic average deviation, ring carbons.
Saturated compounds:—																		
Paraffins: normal	2	0·7	+0·7	8	0·6	−0·5	7	1·1	−1·1	5	1·2	−1·2	0	—	—	22	0·9	−0·7
branched	5	0·7	+0·1	91	1·2	+0·3	20	1·3	−0·2	20	1·0	−0·8	12	1·6	−0·5	148	1·2	0·0
Monocyclopropanes	11	0·7	−0·1	4	1·1	−1·0	0	—	—	0	—	—	0	—	—	15	0·8	−0·3
Monocyclobutanes	6	0·2	+0·1	5	1·0	−0·3	0	—	—	0	—	—	0	—	—	11	0·6	−0·1
Monocyclopentanes	8	0·6	−0·3	40	0·7	−0·3	4	0·2	+0·2	5	0·2	0·0	0	—	—	57	0·6	−0·2
Monocyclohexanes	2	0·6	0·0	58	0·9	+0·1	26	1·4	+1·2	17	0·3	+0·2	4	0·8	+0·8	107	0·9	+0·4
Dicyclopentanes	0	—	—	5	0·7	−0·6	0	—	—	2	1·0	−1·0	0	—	—	7	0·8	−0·7
Decalins	0	—	—	16	1·0	+0·4	7	1·2	+0·8	2	1·2	+1·2	3	1·4	+1·4	28	1·1	+0·7
Dicyclohexanes	0	—	—	5	1·2	−0·6	3	1·0	−0·3	6	1·2	−0·8	0	—	—	14	1·2	−0·6
Condensed tricyclics	0	—	—	2	2·2	+2·2	2	4·5	+4·5	2	1·0	+1·0	0	—	—	6	2·6	+2·6
Tricyclohexanes	0	—	—	0	—	—	4	2·3	−2·3	2	3·3	−3·3	0	—	—	6	2·6	−2·6
Aromatic compounds:—																		
Benzenes	2	0·2	−0·2	132	0·4	+0·3	41	0·5	+0·3	22	0·3	0·0	2	0·2	−0·2	199	0·4	+0·3
Naphthalenes	0	—	—	32	1·4	+1·4	9	1·2	+1·2	3	1·2	+1·2	5	0·9	+0·9	49	1·3	+1·3
Diphenyls	0	—	—	9	1·1	−1·1	21	1·6	−1·6	5	1·9	−1·9	3	1·7	−1·7	38	1·5	−1·5
Condensed tricyclics	0	—	—	3	2·9	+2·9	3	3·8	+3·8	1	2·9	+2·9	0	—	—	7	3·3	+3·3
Triphenyls	0	—	—	0	—	—	5	3·2	−3·2	3	4·0	−4·0	0	—	—	8	3·5	−3·5
Total	36	0·6	0·0	410	0·9	+0·2	152	1·3	+0·1	95	0·9	0·0	29	1·3	0·0	722	0·95	+0·09

TABLE V.

Difference between Calculated and Theoretical Weight per Cent Ring Carbon Atoms for Pure Hydrocarbons.

Molecular-weight range:	<100.			100–200.			200–300.			300–400.			>400.			Total.		
Hydrocarbon type.	No. compounds.	Average deviation, % ring C.	Algebraic average deviation, % ring C.	No. compounds.	Average deviation, % ring C.	Algebraic average deviation, % ring C.	No. compounds.	Average deviation, % ring C.	Algebraic average deviation, % ring C.	No. compounds.	Average deviation, % ring C.	Algebraic average deviation, % ring C.	No. compounds.	Average deviation, % ring C.	Algebraic average deviation, % ring C.	No. compounds.	Average deviation, % ring C.	Algebraic average deviation, % ring C.
Saturated compounds:—																		
Paraffins: normal	2	12	+12	8	6	− 5	7	6	− 6	5	5	− 5	0	—	—	22	6	− 4
branched	5	10	+ 1	91	12	+ 3	20	8	− 1	20	4	− 3	12	4	−1	148	10	+ 1
Monocyclopropanes	11	11	− 2	4	13	−12	0	—	—	0	—	—	0	—	—	15	12	− 4
Monocyclobutanes	6	3	+ 2	5	8	− 3	0	—	—	0	—	—	0	—	—	11	5	0
Monocyclopentanes	8	9	− 4	40	8	− 4	4	2	+ 1	5	1	+ 1	0	—	—	57	7	− 3
Monocyclohexanes	2	8	− 1	58	9	0	26	8	+ 6	17	1	0	4	2	+2	107	7	+ 2
Dicyclopentanes	0	—	—	5	6	− 5	0	—	—	2	4	− 4	0	—	—	7	6	− 5
Decalins	0	—	—	16	8	+ 4	7	7	+ 5	2	6	+ 6	3	5	+5	28	7	+ 4
Dicyclohexanes	0	—	—	5	10	− 5	3	6	− 2	6	5	− 3	0	—	—	14	7	− 4
Condensed tricyclics	0	—	—	2	16	+16	2	24	+24	2	4	+ 4	0	—	—	6	15	+15
Tricyclohexanes	0	—	—	0	—	—	4	12	−12	2	12	−12	0	—	—	6	12	−12
Aromatic compounds:—																		
Benzenes	2	2	− 2	132	3	+ 2	41	3	+ 2	22	1	0	2	0	0	199	3	+ 2
Naphthalenes	0	—	—	32	9	+ 9	9	5	+ 5	3	3	+ 3	5	2	+2	49	7	+ 7
Diphenyls	0	—	—	9	8	− 8	21	9	− 9	5	7	− 7	3	6	−6	38	8	− 8
Condensed tricyclics	0	—	—	3	16	+16	3	15	+15	1	10	+10	0	—	—	7	15	+15
Triphenyls	0	—	—	0	—	—	5	15	−15	3	14	−14	0	—	—	8	15	−15
Total	36	8	0	410	8	+ 2	152	6	0	95	3	− 1	29	4	0	722	6·8	+ 0·06

TABLE VI.

Refractive Index Method of Analysis Applied to Mixed-type Compounds Containing both Aromatic and Naphthenic Rings.

P.S.C. no.	Name of compound.	Mol wt.	Ref. index, n_D^{20}.*	Aromatics.				Naphthenes.			
				Wt-% rings.		No. of rings.		Wt-% rings.		No. of rings.	
				Theoretical.	Calc.†	Theoretical.	Calc.†	Theoretical.	Calc.‡	Theoretical.	Calc.‡
16	α-*n*-Hexadecylhydrindene	342·6	1·4941	22	27	1	1·2	19	60	1	2·9
128	1 : 7-Di*cyclo*pentyl-4(2-phenylethyl)heptane	340·6	1·5070	23	33	1	1·5	40	74	2	3·6
130	1-Phenyl-3(2-*cyclo*hexylethyl)-6-*cyclo*pentylhexane	340·6	1·5086	23	33	1	1·6	45	76	2	3·7
517	1-Phenyl-1-*cyclo*hexylethane	188·3	1·5210	41	55	1	1·4	44	122	1	3·3
521	1-Phenyl-2-*cyclo*hexylethane	188·3	1·5156	41	53	1	1·3	44	118	1	3·1
522	1-Phenyl-3-*cyclo*pentylpropane	188·3	1·5104	41	50	1	1·3	37	112	1	3·0

* Data from A.P.I. Research Project 42.
† Calculated from Equations (43) and (44), considering side chains as paraffins.
‡ Calculated from Equations (4) and (12), considering side chains as paraffins.

equations assume that all rings are six-carbon-atom rings, and some error is introduced when dealing with three-, four-, and five-carbon-atom rings. The effect of excluding the eighty-three compounds of these classes, however, has a negligible effect on the average deviation, which for the 722 hydrocarbons is only $\pm$ 0·16 ring.

The number of carbon atoms occurring in ring structure were calculated by means of Equation (7) for paraffins and naphthenes, and by means of Equation (45) for aromatics. The comparison of the results with the theoretical values is summarized in Table IV. The effect of using the average relations for condensed- and non-condensed-ring compounds is again noticeable. The average deviation for the total of 722 hydrocarbons, however, indicates that the number of ring carbon atoms may be predicted to within about one carbon atom. The algebraic average deviation for the total number of compounds investigated was only + 0·1 carbon atom.

Table V summarizes the results of calculating the weight per cent of total carbon atoms occurring in ring structure by means of Equation (15) for paraffins and naphthenes, and by means of Equation (46) for aromatics, and comparing the values with the theoretical weight per cent ring carbon atoms. Again the effect of using the average relations for condensed- and non-condensed-ring hydrocarbons is noticeable. In the examination of unknown mixtures, however, the use of such equations are justified by the negligible algebraic average deviation of the calculated values from the theoretical weight per cent ring carbon atoms. The arithmetic average deviation for the 722 hydrocarbons was only about $\pm$ 7 per cent ring carbon atoms.

1. *Mixed-type Hydrocarbons.* Where mixed-type compounds containing both aromatic and naphthenic rings are present the method is not strictly applicable. This can be illustrated by the data presented in Table VI, where the method is applied to several compounds of this type which were prepared on A.P.I. Project 42.[13, 14] The equations are derived on the basis that any side chains on the aromatic or naphthenic nuclei are paraffinic, and where this is not true the refractive index of the compound will be increased, resulting in high calculated values for weight per cent rings or number of rings. While it is conceivable that such mixed-type compounds may occur in petroleum fractions and that they would be included with the aromatic portions in silica-gel extractions, the concentration of this type of material in the aromatic fraction may not be sufficiently great to affect seriously the average results. Even with the pure compounds it is noted that the calculated aromatic-ring content is increased over the actual by an amount corresponding to only about one-third of the theoretical naphthenic-ring content and that each naphthene ring causes a rise of only about 0·4 ring in the calculated number of aromatic rings.

2. *Effect of Side-chain Unsaturation.* Unsaturation in the paraffinic side chain also causes some error in the calculated results obtained when applying the proposed method of ring analysis to pure hydrocarbons. The effect of side-chain unsaturation on the calculated results for some compounds prepared under A.P.I. Research Project 42 [14] is illustrated in Table VII. The data on these few compounds indicate that one double bond in the side

TABLE VII.

Effect of Olefinic Unsaturation on the Ring Analysis of Some Hydrocarbons Prepared by A.P.I. Project 42.

P.S.C. no.	Name.	Mol wt.	Refractive index, n_D^{20}.	No. of rings.*		Wt-% rings.*		No. of ring.*		Wt-% ring.*	
				Theoretical.	Calc.	Theoretical.	Calc.	Theoretical.	Calc.	Theoretical.	Calc.
	Paraffins :—										
529	*n*-Tridecane	184·4	1·4256	0	−0·1	0	− 7	0	− 0·9	0	− 7
530	1-Tridecene	182·3	1·4334	0	0·3	0	18	0	2·3	0	18
532	*n*-Pentadecane	212·4	1·4320	0	−0·1	0	− 8	0	− 1·2	0	− 8
533	1-Pentadecene	210·4	1·4388	0	0·3	0	14	0	2·2	0	15
535	*n*-Heptadecane	240·5	1·4366	0	−0·1	0	− 7	0	− 1·2	0	− 7
536	1-Heptadecene	238·4	1·4436	0	0·4	0	14	0	2·1	0	14
25	9-*n*-Octylheptadecane	352·7	1·4487	0	−0·2	0	− 5	0	− 1·0	0	− 5
26	9-*n*-Octyl-8-heptadecene	350·7	1·4554	0	0·5	0	12	0	3·2	0	13
	Naphthenes :—										
90	1 : 5-Di(*cyclo*hexyl-3(2-*cyclo*hexylethyl)pentane	346·6	1·4913	3·0	2·8	72	58	18·0	14·7	72	59
115	1 : 5-Di(*cyclo*hexyl-3(2-*cyclo*hexylethyl)2-pentene	344·6	1·5001	3·0	3·3	72	67	18·0	17·0	72	67
113	1 : 7-Di(*cyclo*pentyl-4(3-*cyclo*pentylpropyl)heptane	346·6	1·4829	3·0	2·3	60	49	15·0	12·4	60	50
112	1 : 7-Di(*cyclo*pentyl-4(3-*cyclo*pentylpropyl)3-heptene	344·6	1·4917	3·0	2·8	60	58	15·0	14·9	60	59
	Aromatics :—										
89	1 : 5-Diphenyl-3(2-phenylethyl)pentane	328·5	1·5725	3·0	2·7	70	56	18·0	14·2	72	59
119	1 : 5-Diphenyl-3(2-phenylethyl)2-pentene	326·5	1·5816	3·0	2·9	71	58	18·0	15·0	72	61
12	1 : 1-Diphenyltetradecane	350·6	1·5202	2·0	1·8	44	37	12·0	10·2	46	39
13	1 : 1-Diphenyl-1-tetradecene	348·6	1·5363	2·0	2·2	44	43	12·0	11·8	46	45
9	11-Phenyleneicosane	372·7	1·4788	1·0	0·9	21	19	6·0	5·6	22	21
52	11-Phenyl-10-eneicosane	370·7	1·4922	1·0	1·2	21	26	6·0	7·3	22	27

* The effect of the olefinic linkage was neglected in the calculations, the compounds being considered as paraffin-naphthene or aromatic according to the listing given in the table.

chain would increase the calculated results by approximately the following amounts :—

	No. of rings.	Wt-% rings.	No. of ring C atoms.	Wt-% C in rings.
Paraffins . . .	0·5	21	3·5	22
Naphthenes . . .	0·5	9	2·4	9
Aromatics . . .	0·3	5	1·0	5

The deviations noted for the effect of a single double bond on naphthenes and aromatics are practically within the experimental variations noted for different hydrocarbons of the same classes. For paraffins alone, however, unsaturation causes an appreciable error, and the error would be expected to increase as unsaturation increases. This can be illustrated by the following data :—

Hydrocarbon.	Molecular weight.	Refractive index, n_D^{20}.	No. of rings.	Wt-% rings.	No. of ring carbon atoms.	Wt-% C in rings.
n-Tridecane . .	184·4	1·4256 [14]	−0·1	−7	−0·9	−7
1-Tridecene . .	182·3	1·4334 [14]	0·3	18	2·3	18
2 : 6-Dimethyl-1 : 8-undecadiene . .	180·3	1·4490 [6]	1·0	44	5·8	45
2 : 6-Dimethyl-1 : 8-10-undecatriene . .	178·3	1·4726 [6]	1·7	76	9·8	77

The above results were computed by means of Figs. 7 and 8. If the unsaturated compounds are considered as "aromatics," the results estimated by means of Figs. 12 and 13 would be approximately one-half the amounts recorded above.

Similarly, errors would be introduced if the methods were applied to cyclic olefins or acetylenes. The extent to which such compounds occur in straight-run petroleum products, however, would not be expected to affect significantly the analysis.

Mixtures of Known Hydrocarbons.

In mixtures of pure hydrocarbons where only naphthenes and paraffins or aromatics and paraffins are present the proposed method of ring analysis should apply with reasonable accuracy. Some comparative data are given in Tables VIII and IX for four series of binary mixtures. The number of rings, weight per cent rings, number of carbon atoms in rings, and weight per cent carbon atoms in rings have been calculated for two series of naphthene–paraffin mixtures in Table VIII and for two series of aromatic–paraffin mixtures in Table IX. Comparison with theoretical values shows the following algebraic deviations :—

	Naphthene–paraffin mixtures.	Aromatic–paraffin mixtures.
No. of rings	−0·2	0
Wt-% rings	+0·4	+4·8
No. of ring carbons . . .	+0·5	+0·5
Wt-% C atoms in rings . .	+0·5	+4·1

TABLE VIII.

Analysis of Two Binary Naphthene–Paraffin Mixtures by Refractive Index and Molecular Weight.

Mol-% paraffin.	Mol wt, M.	Refractive index, n_D^{20}.	No. rings, R_N.		Wt-% rings.		No. ring C, C_N.		Wt-% ring C.	
			Theoretical.	Calc.*	Theoretical.	Calc.†	Theoretical.	Calc.‡	Theoretical.	Calc.§
trans-Decalin–Decane (*Industr. Engng Chem.*, 1950, **42**, 649–53).										
0	138·2	1·4692	2·0	1·7	100	95	10·0	9·5	100	95
10	138·6	1·4624	1·8	1·5	90	86	9·0	8·7	90	87
20	139·0	1·4558	1·6	1·3	80	78	8·0	7·9	80	79
30	139·4	1·4496	1·4	1·2	69	69	7·0	7·0	70	70
40	139·8	1·4436	1·2	1·0	59	61	6·0	6·2	60	62
50	140·2	1·4379	1·0	0·9	49	52	5·0	5·3	50	53
60	140·6	1·4323	0·8	0·7	39	43	4·0	4·4	40	44
70	141·0	1·4269	0·6	0·5	29	34	3·0	3·5	30	34
80	141·4	1·4217	0·4	0·3	20	24	2·0	2·5	20	25
90	141·8	1·4167	0·2	0·2	10	13	1·0	1·3	10	13
100	142·3	1·4120	0·0	−0·1	0	−6	0·0	−0·6	0	−6
Methyl*cyclo*hexane–*n*-heptane (McCormick, M.S. Thesis, The Penna. State College, 1942).										
0	98·2	1·4232	1·0	0·9	85	76	6·0	5·4	86	78
10	98·4	1·4190	0·9	0·8	76	70	5·4	5·0	77	71
20	98·6	1·4151	0·8	0·7	67	62	4·8	4·5	69	64
30	98·8	1·4113	0·7	0·6	59	58	4·2	4·1	60	58
40	99·0	1·4078	0·6	0·5	50	51	3·6	3·6	51	52
50	99·2	1·4043	0·5	0·5	42	44	3·0	3·2	43	45
60	99·4	1·4006	0·4	0·4	33	37	2·4	2·7	34	38
70	99·6	1·3970	0·3	0·3	25	29	1·8	2·1	26	30
80	99·8	1·3938	0·2	0·2	17	22	1·2	1·6	17	23
90	100·0	1·3907	0·1	0·1	8	14	0·6	1·0	9	14
100	100·2	1·3878	0·0	0·0	0	3	0·0	0·2	0	3

* Calculated from Equation (12). ‡ Calculated from Equation (7).
† Calculated from Equation (4). § Calculated from Equation (15).

TABLE IX.

Analysis of Two Binary Aromatic–Paraffin Mixtures by Refractive Index and Molecular Weight.

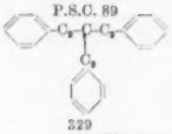
Mol-% paraffin.	Mol wt, M.	Refractive index, n_D^{20}.	No. rings, R_A.		Wt-% rings.		No. ring C, C_A.		% ring C.	
			Theoretical.	Calc.*	Theoretical.	Calc.†	Theoretical.	Calc.‡	Theoretical.	Calc.§
Toluene–*n*-heptane (Bromiley and Quiggle, *Industr. Engng Chem.*, 1933, **25**, 1136).										
0	92·1	1·4966	1·0	1·0	84	81	6·0	5·8	86	83
10	92·9	1·4813	0·9	0·9	75	74	5·4	5·3	77	76
20	93·7	1·4676	0·8	0·8	66	66	4·8	4·8	69	69
30	94·5	1·4550	0·7	0·7	57	59	4·2	4·3	60	61
40	95·3	1·4434	0·6	0·6	49	52	3·6	3·8	51	54
50	96·1	1·4322	0·5	0·5	40	45	3·0	3·3	43	47
60	96·9	1·4218	0·4	0·4	32	38	2·4	2·8	34	40
70	97·8	1·4124	0·3	0·3	24	30	1·8	2·3	26	32
80	98·6	1·4034	0·2	0·2	16	22	1·2	1·7	17	24
90	99·4	1·3951	0·1	0·1	8	14	0·6	1·1	9	15
100	100·2	1·3878	0·0	0·0	0	2	0·0	0·2	0	2
Methylnaphthalene–cetane (Tegge, M.S. Thesis, The Penna. State College, 1940).										
0	142·2	1·6073	2·0	2·0	89	98	10·0	11·0	91	99
10	150·6	1·5740	1·8	1·8	76	84	9·0	9·9	78	81
20	159·0	1·5470	1·6	1·6	64	72	8·0	8·9	67	70
30	167·5	1·5246	1·4	1·4	53	61	7·0	8·0	56	63
40	175·9	1·5050	1·2	1·2	43	51	6·0	7·0	46	53
50	184·3	1·4895	1·0	1·0	34	42	5·0	6·1	37	45
60	192·7	1·4758	0·8	0·8	26	34	4·0	5·1	29	37
70	201·1	1·4635	0·6	0·6	19	27	3·0	4·1	21	28
80	209·6	1·4527	0·4	0·5	12	19	2·0	3·1	13	20
90	218·0	1·4433	0·2	0·2	6	11	1·0	1·8	6	12
100	226·4	1·4349	0·0	−0·1	0	−3	0·0	−0·5	0	−3

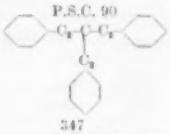
* Calculated from Equation (44). ‡ Calculated from Equation (45).
† Calculated from Equation (43). § Calculated from Equation (46).

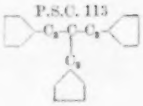
TABLE X.—*Analysis of Mixtures of Hydrocarbons.*
(Data from Schiessler *et. al.*[14])

Parent hydrocarbons used in mixtures :—

P.S.C. 25

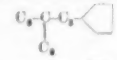
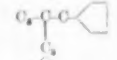
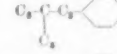
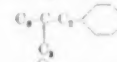
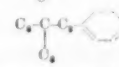
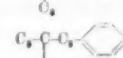
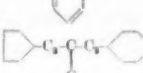
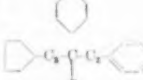
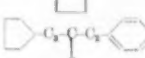
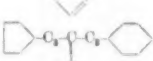
P.S.C. 89 

P.S.C. 90 

P.S.C. 115 

	P.S.C. 25	P.S.C. 89	P.S.C. 90	P.S.C. 115
Mol. wt . .	353	329	347	347
n_D^{20} . . .	1·4487	1·5725	1·4913	1·4839

Pure hydrocarbons and physical mixtures of above to match average composition :—

P.S.C. no.*		Mol. wt.	n_D^{20}.	No. naphthene rings.		Wt-% naphthene rings.	
				Theoretical.	Calc.†	Theoretical.	Calc.†
110		351	1·4592	1	0·8	20	20
25_2–113_1		351	1·4595	1	0·8	20	20
111		349	1·4707	2	1·6	40	34
25_1–113_2		349	1·4708	2	1·6	40	34
88		351	1·4614	1	0·9	24	22
25_2–90_1		351	1·4619	1	1·0	24	23
19		349	1·4756	2	1·9	48	40
25_1–90_2		349	1·4760	2	1·9	48	41
87		345	1·4806	1 ‡	1·0 §	22 ‡	22 §
25_2–89_1		345	1·4813	1 ‡	1·0 §	22 ‡	22 §
18		337	1·5192	2 ‡	1·8 §	46 ‡	37 §
25_1–89_2		**337**	**1·5213**	**2 ‡**	**1·8 §**	**46 ‡**	**38 §**
129		347	1·4858	3	2·5	64	52
90_1–113_2		347	1·4859	3	2·5	64	52
127		347	1·4886	3	2·6	68	55
90_2–113_1		347	1·4886	3	2·6	68	55
128		341	1·5070	2 + 1 ‡	3·6 (1·6) ‡	40 (23) ‡	74 (33) §
89_1–113_2		341	1·5082	2 + 1 ‡	3·7 (1·6) §	40 (23) ‡	75 (33) §
126		335	1·5354	1 + 2 ‡	— (2·1) §	21 (46) ‡	— (45) §
89_2–113_1		335	1·5377	1 + 2 ‡	— (2·1) §	21 (46) ‡	— (44) §
130		341	1·5086	2 + 1 ‡	3·7 (1·6) §	45 (23) ‡	76 (33) §
89_1–90_1–113_1		341	1·5111	2 + 1 ‡	3·9 (1·6) §	45 (23) ‡	78 (34) §

* Mixtures are indicated by the two or more numbers of the hydrocarbons mixed, the subscripts referring to the number of moles present in the mixture.
‡ Aromatic rings.
† By Fig. 7.
§ Calculated as entirely aromatic rings, Fig. 13.

Some further comparisons of theoretical and calculated ring analysis data for ten binary mixtures and one ternary mixture prepared to have the same average compositions, with respect to rings and side chains, as certain pure hydrocarbons [14] are given in Table X. The data indicate reasonable agreement between calculated and actual number of rings and weight per cent rings as long as the ring portions are entirely naphthenic or entirely aromatic. As mentioned previously, however, when both aromatic and naphthene rings are present the system of ring analysis is not particularly accurate.

Several other ternary mixtures of aromatic hydrocarbons were also prepared and the refractive index measured. These were then examined by the ring-analysis procedure, and the results are presented in Table XI. It will be noted that excellent agreement was found between the calculated and the theoretical values in all of these cases. It is also of interest to

TABLE XI.

Analysis of Several Ternary Aromatic Mixtures by Refractive Index and Molecular Weight.

	Blend No. 1.		Blend No. 2.		Blend No. 3.		Blend No. 4.	
	Wt-%.	Mol-%.	Wt-%.	Mol-%.	Wt-%.	Mol-%.	Wt-%.	Mol-%.
Composition :—								
Diamylbenzene	30·2	26·5	—	—	58·3	53·8	—	—
Monoamylnaphthalene	34·2	33·0	—	—	21·3	21·7	—	—
Diphenylmethane	35·6	40·5	34·7	34·3	20·4	24·5	15·0	16·7
Nonylbenzene	—	—	29·9	24·3	—	—	74·9	68·7
α-Methylnaphthalene	—	—	35·4	41·4	—	—	11·1	14·6
Properties :—								
Molecular weight, M	191		166		202		189	
Refractive index, n_D^{20}	1·5443		1·5612		1·5178		1·5117	
Number of rings, R_A:—								
Theoretical	1·7		1·8		1·5		1·3	
Calc *	1·7		1·8		1·4		1·3	
Wt-% rings :—								
Theoretical	65		73		53		52	
Calc †	63		75		51		51	
No. ring carbons, C_A:—								
Theoretical	9·8		9·6		8·3		7·6	
Calc ‡	9·5		9·8		8·0		7·5	
Wt-% ring carbons :—								
Theoretical	68		76		55		54	
Calc §	66		77		53		53	

* Calculated from Equation (44). ‡ Calculated from Equation (45).
† Calculated from Equation (43). § Calculated from Equation (46).

point out here that since these tenrary mixtures contain only benzenes, diphenyls, and naphthalenes, the concentration of the latter may be estimated from the number of rings and the number of carbon atoms in ring structure by the following relation :—

$$\text{Mol-\% naphthalenes} = 300\ (\text{no. of rings}) - 50\ (\text{no. C atoms in rings})$$

Using this equation and the calculated values given in Table XI the results for the four blends are summarized as follows :—

Blend no.	Mol-% naphthalenes	
	calc.	actual.
1	35	33
2	50	41
3	20	22
4	15	15

The agreement here is good, probably due to the fact that diphenyls and naphthalenes were present in the mixtures in about equal proportions. Ordinarily, this method cannot be expected to give accurate results.

Petroleum Fractions.

As previously mentioned, the application of the proposed method of ring analysis to petroleum products requires the preliminary separation into paraffin–naphthene and aromatic portions by some suitable process. The significance which can be attached to the ring-analysis data obtained on these classes of hydrocarbons is then somewhat dependent on the boiling range of the original petroleum fraction, since only average values are given. In materials as complex as petroleum the ring-analysis data on wide-boiling-range fractions yields very limited information regarding the composition. If a systematic scheme of separation by fractional distillation and extraction or adsorption is followed so that materials of relatively narrow-molecular-weight ranges are segregated, the application of the ring-analysis procedure to these portions yields results which have much more significance in connexion with the chemical composition of the fractions.

1. *Gas-oil Fractions.* In order to illustrate the application of the ring-analysis method to kerosine and gas-oil fractions, reference is made to the separation of a kerosine–gas-oil fraction from a Pennsylvania crude oil by distillation and vapour–liquid extraction. By these processes certain products were prepared which consisted essentially of concentrates of paraffinic or aromatic materials in relatively narrow-boiling-point ranges. The ring-analysis results obtained on some of the products on which reasonably sharp separations according to classes of hydrocarbons had been effected are given in Table XII, together with some of the average physical properties and the composition estimated empirically from boiling points, refractive indices, and sulphuric acid extraction data. This latter method of analysis is not strictly comparable to the molecular-weight–refractive-index method because it is an estimate of the volume per cent of the total paraffins, naphthenes, and aromatics (side chains being included with the rings to which they are attached), while the former refers only to the ring portions (side chains not being included with the rings).

An estimate of the total naphthenes and aromatics present in the products can be obtained from the average number of rings calculated only if certain assumptions regarding the size and type of the rings that could be present are made. For example, if the naphthenes in Product 15, having an average number of rings of 0·4, are assumed to be *cyclo*hexane derivatives the total naphthenes present would be about 40 weight per cent, compared to 23 volume per cent computed by the other procedure. In general, such extended treatment of the results is not recommended because of its sensitivity to minor variations in the analyses. The presence of certain compounds tending to increase the average refractive index out of proportion to its concentration, such as would occur if small amounts of aromatics were present, may also affect the calculated ring analysis disproportionally.

In the case of the aromatic concentrates, if the products are assumed to be 100 per cent aromatics, the number of rings then gives some indication of the relative proportions of monocyclic and dicyclic aromatics. For example, Product 17, having an average of 1·4 rings per molecule, would

appear to be composed of 40 per cent dicyclic aromatics and 60 per cent monocyclic aromatics. The limitations mentioned above are applicable to a lesser degree. Additional information is required, however, to determine whether the dicyclic aromatics are naphthalene derivatives or biphenyl derivatives, or whether other types of hydrocarbons might be grouped with the aromatics by the separational process.

TABLE XII.

Analysis of Fractions from Pennsylvania Kerosine and Gas Oil Separated by Distillation and Vapour–Liquid Extraction.

Product no.	Estimated ref. index, $n_D^{20.0}$*	Estimated mol. wt.†	Approx. no. of carbon atoms.	Estimated composition.‡			Naphthene rings.§		Aromatic rings.¶	
				Vol-% paraffins.	Vol-% naphthenes.	Vol-% aromatics.	Wt-%.	No.	Wt-%.	No.
15	1·4330	172	12 to 13	77	23	0	23	0·4	—	—
17	1·5396	142	10 to 11	0	0	100	—	—	74	1·4
18	1·4262	182	13	100	0	0	0	0	—	—
19	1·4278	182	13	90	10	0	3	0·1	—	—
21	1·4304	180	13	92	8	0	12	0·2	—	—
23	1·5282	156	11 to 12	0	0	100	—	—	65	1·4
24	1·4362	190	13 to 14	83	17	0	20	0·4	—	—
26	1·5489	160	12	0	0	100	—	—	72	1·6
27	1·4299	200	14	100	0	0	0	0	—	—
28	1·4371	204	14 to 15	85	15	0	14	0·3	—	—
30	1·5310	176	13	0	0	100	—	—	61	1·5
31	1·4396	212	15	87	13	0	16	0·3	—	—
33	1·5407	182	13 to 14	0	0	100	—	—	64	1·6
34	1·4468	220	15 to 16	71	29	0	26	0·6	—	—
36	1·5182	188	14	0	5	95	—	—	54	1·4

* Average of values for fractions combined.
† From boiling point and refractive index (Fig. 1).
‡ From acid-extraction data and physical properties (Report No. P.R.L.-2–48, p. 10).
§ Using Fig. 7.
¶ Using Fig. 12.

2. *Lubricating Oil Extraction Fractions.* Since the molecular-weight–refractive-index method of analysis yields values which are similar to those obtained by the Waterman analysis [16] for hydrocarbon types, it is of interest to compare the results on a series of oil fractions obtained by the solvent fractionation of a Pennsylvania 180 neutral. In the process the aromatic hydrocarbons are concentrated in the first few fractions, and after the aromatics have been removed the process tends to separate the hydrocarbons more or less on the basis of molecular size, particularly when using acetone as the solvent. Comparative results for the analysis of the first three aromatic fractions and the last fourteen aromatic-free fractions derived from the neutral stock are shown in Table XIII. It will be noted that for the aromatic portions, the weight per cent rings calculated by the molecular-weight–refractive-index method are approximately equal to the total of aromatic and naphthene rings given by the Waterman procedure. This tendency would be expected if the initial separation was not complete. The average number of aromatic rings calculated by the molecular-weight–refractive-index method reciprocally are slightly lower than the corresponding values given by the Waterman procedure.

For the naphthene–paraffin fractions the molecular-weight–refractive-index method yields slightly higher values for number of naphthene rings and weight per cent rings than is calculated by the Waterman procedure. These differences are undoubtedly due to the different methods of treating the basic data on pure hydrocarbons. The Waterman procedure is based on the assumption that all of the polycyclic naphthenes are present as

TABLE XIII.

Analysis of Solvent-extraction Fractions from a Pennsylvania 180 Neutral.

(Data from paper presented at Petroleum Div., Amer. Chem. Soc. Meeting, Baltimore, April 3–7, 1939.)

Fraction no.	Mol. wt.	Refractive index, n_D^{20}.	Wt-% rings (Waterman).		Wt-% rings (M–n_D^{20} method).		Average no. of rings.	
			Aromatic.	Naphthene.	Aromatic.	Naphthene.	Waterman.	M–n_D^{20}.
1	335	1·5460	44	2	47	—	2·6	2·3
2	337	1·5390	40	4	45	—	2·55	2·15
3	347	1·5200	29	13	37	—	2·4	1·8
9	377	1·4755	0	24	—	37	1·5	1·85
10	374	1·4737	0	23	—	36	1·45	1·75
11	379	1·4723	0	21	—	33	1·35	1·65
12	379	1·4717	0	21	—	33	1·35	1·6
13	393	1·4706	0	21	—	30	1·35	1·5
14	393	1·4702	0	21	—	30	1·3	1·5
15	402	1·4702	0	19	—	29	1·3	1·5
16	415	1·4701	0	19	—	27	1·3	1·45
17	418	1·4701	0	18	—	27	1·25	1·45
18	435	1·4701	0	17	—	26	1·25	1·45
19	448	1·4701	0	17	—	25	1·25	1·4
20	459	1·4701	0	17	—	24	1·25	1·4
21	473	1·4701	0	16	—	23	1·25	1·4
Residue	506	1·4717	0	15	—	23	1·3	1·5

Data on Original Neutral :—

Gravity, ° A.P.I.	30·2
Viscosity at 100° F, S.U.S.	185·6
Viscosity Index	100
Refractive Index, n_D^{20}	1·4848
Aniline Point, ° C	100·4

Separation of the successive fractions was accomplished by reflux batch extraction at 25° C using acetone as the solvent.

six-carbon-atom condensed rings, while the molecular-weight–refractive-index method is based on the average values for condensed- and non-condensed-ring compounds. Further data would be necessary to determine more exactly the types and structure of hydrocarbons present in complex mixtures such as lubricating oils.

COMPARISON OF RESULTS WITH OTHER METHODS OF ANALYSIS.

Although the data presented in the previous section provide a critical analysis of the relative value of the proposed method of ring analysis, it is of interest to compare the results that are obtained with those that would

be given when employing some of the procedures that have been suggested by other investigators. In this survey the comparisons will be restricted to data on pure compounds, since then a more accurate evaluation of the various methods may be obtained.

Density Coefficient–Density Method.

A method for the analysis of ring content in mixtures of paraffins and naphthenes which is similar to the molecular-weight–refractive-index method has been suggested by Lipkin, Martin, and Kurtz.[9] Their method is based on the correlations of the temperature coefficient of density and either density or refractive index of pure hydrocarbons. Since their density coefficient is approximately equal to the reciprocal of the molecular weight within experimental error, it would be expected that the methods should show reasonable agreement with each other. This is confirmed by the summarized comparison of results on pure hydrocarbons shown in Table XIV.

TABLE XIV.

Comparison of Methods of Analysis for Pure Hydrocarbons.
(Paraffins and Naphthenes.)

Hydrocarbon series.	Lipkin, Martin, and Kurtz.[9]					M–n_D^{20} method.‡	
	No. of compounds.	A–d.*	A–n.†	Davis and McAllister.[5]	Waterman.[16]	No. of compounds.	M–n_D^{20}.
Arithmetic average deviation of calc wt-% ring carbon atoms.							
Paraffins	224	7	7	9	6	170	9
Monocyclopentanes	56	6	9	11	5	57	7
Monocyclohexanes	115	8	9	10	11	107	7
Dicyclopentanes	7	2	5	6	6	7	6
Dicyclohexanes	26	5	7	7	21	14	7
Decalins	32	6	5	9	8	28	7
Tricyclics	13	10	10	9	18	12	14
Algebraic average deviation of calc wt-% ring carbon atoms.							
Paraffins	224	0	0	6	3	170	0
Monocyclopentanes	56	−2	−7	−7	− 2	57	−4
Monocyclohexanes	115	1	1	−1	−10	107	2
Dicyclopentanes	7	−1	−4	−2	− 4	7	−5
Dicyclohexanes	26	−4	2	2	−17	14	−4
Decalins	32	5	6	8	− 7	28	4
Tricyclics	13	−3	−2	4	−12	12	2

* Refers to method using density coefficient, A, and density, d [9].
† Refers to method using density coefficient, A, and refractive index, n[9].
‡ Data from Table V.

Lipkin, Martin, and Kurtz recorded the average deviations from theoretical values of their results calculated by the density coefficient–density method,[9] the density-coefficient–refractive-index method,[9] the method of Davis and McAllister,[4] and the Waterman procedure [16] for a large number of pure paraffins and naphthenes. Their weight per cent rings refer to " 100 times the ratio of the ring carbon atoms to the total

carbon atoms." These authors also list " deviations of average " which presumably refers to the algebraic average deviations. In the comparisons shown in Table XIV it will be noted that the proposed molecular-weight–refractive-index method (M–n_D^{20}) shows approximately the same deviations as the density-coefficient–density and the density-coefficient–refractive-index methods, and that either of these methods are more accurate than the results obtained by the Davis and McAllister or Waterman procedure for pure hydrocarbons. The number of compounds examined by the investigators in this survey differ only slightly, but it should not be concluded that identical compounds were always included in each group.

Lipkin and Martin [10] also applied a density-coefficient–density-method to the analysis of aromatics for estimating the weight per cent ring carbon atoms and the number of aromatic rings. A comparison of their results obtained when using correlations based on mixtures of condensed- and non-condensed-ring compounds to those obtained by the proposed molecular-weight–refractive-index method is summarized in Table XV. Again

TABLE XV.

Comparison of Methods of Analysis for Pure Hydrocarbons (Aromatics).

Aromatic series.	Lipkin and Martin.[10] *			M–n_D^{20} method.†		
	No. of compounds.	Arithmetic average deviation.	Algebraic average deviation.	No. of compounds.	Arithmetic average deviation.	Algebraic average deviation.
	Wt-% ring carbon atoms.					
Monocyclic	221	3	0	199	3	+ 2
Condensed dicyclic	41	4	+4	49	7	+ 7
Non-condensed dicyclic	30	5	−5	38	8	− 8
Condensed tricyclic	6	9	+9	7	15	+15
Non-condensed tricyclic	1	9	−9	8	15	−15
	Number of rings per molecule.					
Monocyclic	221	0·1	0	199	0·1	0
Condensed dicyclic	41	0·1	−0·1	49	0·1	+ 0·1
Non-condensed dicyclic	30	0·1	0	38	0·1	− 0·1
Condensed tricyclic	6	0·1	0	7	0·3	+ 0·3
Non-condensed tricyclic	1	0	0	8	0·2	− 0·2

* Method using density coefficient and density for mixtures of condensed- and non-condensed-ring romatics.

† Data from Tables III and V.

the accuracy of the two methods is about equal, except that the molecular-weight–refractive-index method tends to show greater variations for condensed and non-condensed tricyclic aromatics than does the density-coefficient–density method. As pointed out previously, this is due to the fact that for the same molecular weight and the same number of rings per molecule the condensed-ring aromatics have higher refractive indexes than the corresponding non-condensed-ring aromatics (*cf.* Fig.3), while this " reversal " is not as pronounced when density is used in place of refractive index.

Davis and McAllister Method.

Some data were presented above on the application of the Davis and McAllister method [4] to pure hydrocarbons. These investigators proposed the following formula for estimating the number of carbon atoms per molecule combined in naphthene rings :—

$$N = (0{\cdot}358)\ (\text{mol wt}) + 7{\cdot}7 - (0{\cdot}3)\ (\text{mol vol})$$

Fair agreement between calculated and theoretical weight per cent ring carbon atoms is indicated by the data shown in Table XIV when using this procedure on pure naphthenes. However, the majority of the compounds examined were probably of relatively low molecular weight. The above formula was also tested on a number of relatively high-molecular-weight hydrocarbons and mixtures by Schiessler *et al.*[13] These results are presented in Table XVI, together with the values calculated by the molecular-weight–refractive-index method using Fig. 8. It will be noted that the

TABLE XVI.

Number of Carbon Atoms per Molecule in Naphthene Rings Calculated by Several Procedures.

P.S.C. no.	Hydrocarbon.	Mol. wt, *M*.	Refractive index, n_D^{20}.	Carbon atoms in naphthene rings.		
				Theoretical.	Davis and McAllister.[4]	$M-n_D^{20}$.*
1	11-*n*-Butyldocosane	367	1·4500	0	2·3	−1·2
22	6 : 11-Di-*n*-amylhexadecane	367	1·4502	0	2·9	−1·0
23	2-Ethyl-5(2-ethylbutyl)-octadecane	367	1·4521	0	3·5	−0·6
55	5 : 14-Di-*n*-butyloctadecane	367	1·4508	0	2·9	−0·3
63	9-*n*-Octyleicosane	395	1·4515	0	2·4	−1·1
67	11-Neopentylheneicosane	367	1·4491	0	2·0	−1·6
64	11-*cyclo*Pentylheneicosane	365	1·4613	5	7·0	5·3
60	11-*cyclo*Hexylheneicosane	379	1·4639	6	7·8	6·3
69	13-*cyclo*Hexylpentacosane	435	1·4653	6	8·0	6·3
76	5-*cyclo*Hexyleicosane	365	1·4638	6	7·6	6·4
78	9-*cyclo*Hexyleicosane	365	1·4635	6	7·5	6·3
62	11-α-Decalinheneicosane	433	1·4778	10	13·2	11·2
11	1 : 1-Di*cyclo*hexyltetradecane	362	Solid	12	12·5	—
19	1-*cyclo*Hexyl-3(2-*cyclo*hexylethyl)-hendecane	349	1·4756	12	11·7	10·3
65	1-*cyclo*Hexyl-2(*cyclo*hexylmethyl)-pentadecane	391	1·4747	12	11·8	10·1
505	1 : 1-Di*cyclo*hexylheptane	265	1·4822	12	12·5	11·8
	Mixture : 75 mol-% P.S.C. 63 25 mol-% P.S.C. 65	394	1·4570 †	3	4·8	3·0
	Mixture : 50 mol-% P.S.C. 63 50 mol-% P.S.C. 65	393	1·4626 †	6	7·4	5·5
	Mixture : 25 mol-% P.S.C. 63 75 mol-% P.S.C. 65	392	1·4685 †	9	9·4	8·0
	Mixture : 75 mol-% P.S.C. 67 25 mol-% P.S.C. 78	367	1·4525 †	1·5	3·5	1·1
	Mixture : 50 mol-% P.S.C. 67 50 mol-% P.S.C. 78	366	1·4561 †	3	4·9	3·1
	Mixture : 25 mol-% P.S.C. 67 75 mol-% P.S.C. 78	365	1·4598 †	4·5	6·4	4·9

* Calculated by means of Fig. 8.
† Calculated from values for components assuming linear additivity on a volume-fraction basis.

latter method yields more accurate results than the Davis and McAllister method for practically all of the pure hydrocarbons and binary mixtures

examined. The negative values recorded for the branched paraffins merely indicate that the points for these hydrocarbons fall to the left of the average line for all paraffins on Fig. 8, indicating the extent of variation of the data on branched paraffins. The negative values have no significance, and ordinarily would be reported as zero.

Schiessler *et al* [13] introduced a correction chart for the Davis and McAllister method, but it is possible that such a correction would apply only in the case of relatively high-molecular-weight hydrocarbons. The corrections necessary for low-molecular-weight compounds appears to be in the opposite direction from that suggested by Schiessler, as will be noted from the following data :—

Hydrocarbon.	No. C atoms per molecule in naphthene rings.			
	Theoretical.	Davis and McAllister.	Davis and McAllister corr.	M–n_D^{20} method.
n-Hexane	0	−0·7	?	0·5
n-Decane	0	−1·3	?	−0·5
*cyclo*Hexane	6	5·4	3·5	6·5
Methyl*cyclo*hexane	6	4·6	2·6	5·4
Ethyl*cyclo*hexane	6	5·1	3·2	5·8
Propyl*cyclo*hexane	6	5·1	3·2	5·8
Butyl*cyclo*hexane	6	5·4	3·5	5·8
cis-Decalin	10	11·0	10·8	11·0
trans-Decalin	10	9·5	8·8	9·5
Di*cyclo*hexyl	12	10·7	10·4	10·9
Di*cyclo*hexylmethane	12	10·4	10·0	10·3
1 : 1-Di*cyclo*hexylethane	12	11·9	11·9	11·8

Since Davis and McAllister proposed their method (in 1930), a considerably larger quantity of data on pure hydrocarbons has been made available, and it should be possible to develop a more accurate method employing the same principles. The final equation, of course, is likely to be more complex than the present version.

Waterman Analysis.

Brief comparisons of the results obtained by the proposed molecular-weight–refractive-index method of ring analysis to those obtained by the procedure proposed by Vlugter, Waterman, and Van Westen [16] have been presented in previous sections (Tables XIII and XIV). For oil fractions and for pure compounds the weight per cent naphthene rings calculated by the Waterman procedure were consistently lower than those indicated by the molecular-weight–refractive-index method.

A more critical survey of the Waterman procedure as applied to pure hydrocarbons is given in Table XVII, where the results are calculated for a number of high-molecular-weight aromatics and the corresponding naphthenes. The aromatic ring contents computed by the Waterman procedure are all considerably higher than the theoretical values, and the calculated naphthene-ring contents are appreciably lower than the actual

values. The Waterman calculation of weight per cent aromatic rings is made by multiplying the difference in aniline point caused by hydrogenation of the aromatic by the factor 0·85. Their method of estimating this aniline-point rise on hydrogenation is to multiply the difference between the actual aniline point of the substance and the aniline point corresponding to a paraffinic–naphthenic mixture of the same molecular weight and specific refraction, as determined from their chart, by the factor 0·8. The calculated aniline-point rises for the aromatics listed in Table XVII are slightly lower than the actual aniline-point rises noted for hydrogenation of the aromatic rings. Multiplying these calculated values by a factor 0·51 or multiplying the actual values by a factor 0·45 would yield aromatic ring contents agreeing with the theoretical values within ± 1 per cent aromatic ring. Using the factor of 0·45 together with the calculated aniline-point rises gives values for weight per cent aromatic rings that are only about 2 per cent rings lower than the theoretical values. The source of error in the Waterman procedure when applied to pure hydrocarbons appears to be not so much in the method of estimating the aniline-point rise on hydrogenation as in the choice of the factor 0·85 for conversion to per cent aromatic rings. However, as pointed out by Sachanen,[12] this factor appears to vary with length of side chains and type of rings, and the approximate value of the factor 0·85 obtained by Waterman on the basis of experimentation with lubricating oils may be reasonably accurate for polycyclic aromatics having comparatively short side chains. For aromatics in the kerosine and gas-oil region the factor may need to be even higher.

The number of rings per molecule and the weight per cent naphthene rings are determined by the Waterman procedure from the specific refraction of the completely hydrogenated material. The number of aromatic rings calculated by the Waterman procedure are considerably higher than the theoretical values, while the calculated number of naphthene rings are approximately correct. The error may lie in the method of determining the specific refraction of the hydrogenated material from the molecular weight and the calculated aniline point of the hydrogenated compounds using the factor 0·8 as mentioned above. Using a larger factor here, such as about 0·9, would give better agreement for the data in Table XVII on aniline-point rises and calculated number of aromatic rings for the monocyclic aromatics, but would result in introducing major errors for polycyclic aromatics.

The discrepancies noted in the calculated weight per cent naphthene rings may be due to the fact that the Waterman system is constructed on condensed-ring structures. The effects of other types of structures on the basic assumptions have been discussed by Grosse.[8] The above discussion illustrates some of the disadvantages of applying the Waterman procedure to the analysis of pure hydrocarbons. Some of these disadvantages may also apply when using the system for the analysis of petroleum fractions which have been separated into narrow ranges of molecular size and type.

Other Procedures.

Several other systems of partial ring analysis of hydrocarbon systems have been proposed, but most of these have the disadvantage of requiring

TABLE XVII

Comparison of Ring Analysis Data Obtained by the Waterman Procedure and the Molecular-weight–Refractive-index Method.

P.S.C. no.[13]	Hydrocarbon.	Mol. wt.	Refractive index, n_D^{20}.	Specific refraction.	Aniline point, °C.	Aniline-point rise on hydrogenation.		Calc ring analysis.								
								Theoretical values.			Waterman analysis.[16]			M–n_D^{20} method.†		
						Actual.	Waterman.*	Wt-% aromatic rings.	Wt-% naphthene rings.	No. of rings per molecule.	Wt-% aromatic rings.	Wt-% naphthene rings.	No. of rings per molecule.	Wt-% aromatic rings.	Wt-% naphthene rings.	No. of rings per molecule.
87	9(2-Phenylethyl) heptadecane	345	1·4806	0·3323	53·1	51·7	46·2	22	0	1·0	39	− 3	2·1	22	—	1·0
88	9(2-*cyclo*Hexylethyl)heptadecane	351	1·4614	0·3299	104·8	—	—	0	24	1·0	2	15	1·0	—	23	0·9
99	1-Phenyleicosane	359	1·4801	0·3327	58·9	51·9	43·4	22	0	1·0	37	− 4	2·0	21	—	1·0
100	1-*cyclo*Hexyleicosane	365	1·4623	0·3306	110·8	—	—	0	23	1·0	0	12	0·8	—	22	1·0
101	2-Phenyleicosane	359	1·4795	0·3320	57·6	51·4	43·8	22	0	1·0	37	− 2	2·1	21	—	0·9
102	2-*cyclo*Hexyleicosane	365	1·4640	0·3297	109·0	—	—	0	23	1·0	1	15	1·0	—	24	1·1
103	4-Phenyleicosane	359	1·4794	0·3320	61·0	46·3	41·0	22	0	1·0	35	1	2·2	21	—	0·9
104	4-*cyclo*Hexyleicosane	365	1·4639	0·3292	107·3	—	—	0	23	1·0	1	17	1·0	—	24	1·1
80	5-Phenyleicosane	359	1·4796	0·3321	61·4	45·6	40·7	22	0	1·0	35	− 2	2·0	21	—	0·9
76	5-*cyclo*Hexyleicosane	365	1·4638	0·3295	107·0	—	—	0	23	1·0	2	15	1·0	—	24	1·1
81	7-Phenyleicosane	359	1·4794	0·3325	62·2	44·5	40·6	22	0	1·0	35	− 3	1·9	21	—	0·9
77	7-*cyclo*Hexyleicosane	365	1·4635	0·3295	106·7	—	—	0	23	1·0	2	16	1·1	—	23	1·0
9	11-Phenylheneicosane	373	1·4788	0·3322	66·2	42·3	38·5	21	0	1·0	33	− 2	2·0	19	—	0·9
60	11-*cyclo*Hexylheneicosane	379	1·4639	0·3294	108·5	—	—	0	22	1·0	2	15	1·1	—	24	1·1
54	11-Benzylheneicosane	387	1·4838	0·3328	61·8	46·3	44·0	20	0	1·0	37	− 4	2·1	21	—	1·0
91	11-*cyclo*Hexylmethylheneicosane	393	1·4636	0·3294	108·1	—	—	0	21	1·0	1	14	1·0	—	22	1·0
78	13-Phenylpentacosane	429	1·4787	0·3320	79·4	36·1	32·6	18	0	1·0	28	− 2	1·9	17	—	0·9
69	13-*cyclo*Hexylpentacosane	435	1·4635	0·3297	115·5	—	—	0	19	1·0	1	13	1·0	—	20	1·0
17‡	5-Naphthyldocosane	437	1·5189	0·337	45·6	65·5	64·4§	29	0	2·0	55	−22	2·4	33	—	2·0
39‡	5-Decalindocosane	447	1·4790	0·3281	111·1	—	—	0	26	2·0	3	18	1·7	—	35	2·1

* Calculated by the Waterman procedure as 0·8 times the difference between the measured aniline point and the aniline point read from their molecular-weight-specific-refraction chart.

† Using Fig. 7 for the naphthenes and Fig. 12 for the aromatics.

‡ These compounds were prepared by Mikeska [11]; refractive index corrected from 25° C.

§ Estimated by extrapolation of Waterman's chart.

elaborate or tedious analytical data. A procedure for determining accurately the number of rings per molecule in saturated oils was suggested by Grosse.[8] This method is based on the correlation of the hydrogen-to-carbon (H : C) ratio and the number of carbon atoms per molecule; that is, from careful ultimate analysis data and the molecular weight of the substance it is possible to obtain the empirical formula. The number of naphthene rings, therefore, is given by the relation :—

$$R_N = 2 \text{ (no. C atoms)} + 2 - \text{(no. H atoms)}$$

This method yields precise results on all types of complex saturated cyclic systems whose ring system can be represented on a plane provided that reliable ultimate analysis data are available. The method cannot be extended to determination of the percentages of paraffinic and naphthenic carbons without a knowledge of the structure of the naphthenes present.

Deanesly and Carleton [5] also suggested a system similar to the Waterman analysis but eliminating aniline point and using density, refractive index, specific dispersion, molecular weight, and weight per cent hydrogen. The latter item again requires an elaborate ultimate analysis of the sample, and if these data are available it would appear that a less-complex system could be devised. These authors first correlated specific refraction and weight per cent hydrogen for pure saturated hydrocarbons, the relation found being as follows :—

$$r = 0{\cdot}2084 + 0{\cdot}008421y$$

where r is specific refraction (Lorenz–Lorentz) and y is the weight per cent hydrogen. When double-bond unsaturation occurs, as in aromatics, the equation is corrected by an additional term representing the increment of the refraction due to double bonds. The authors express this increment in terms of the unsaturation in grams of hydrogen per 100 grams of sample, h, and a function k which varies with the nature of the unsaturates and is evaluated by means of the specific dispersion, $S = (n_F - n_C)10^4/d$. The first step is the determination of h from relations which can be combined into the expression :—

$$h = \left[\frac{248{\cdot}6r - 2{\cdot}0935y - 51{\cdot}81}{(S - 98)^{0{\cdot}292}}\right]^{1{\cdot}412}$$

Having this value, the number of rings per molecule, R, is computed as follows :—

$$R = 1 - \frac{Mh}{201{\cdot}6} + \frac{M}{24{\cdot}212}(2{\cdot}016 - 0{\cdot}14026y)$$

Applying this system to several of the monocyclic aromatics prepared under A.P.I. Research Project 42,[3] and using the theoretical weight per cent hydrogen, yields the following results :—

P.S.C. no.	Hydrocarbon.	Measured.				Calc.		
		M.	y.	r.	S.	h.	R.	A.
9	11-Phenylheneicosane	373	12·98	0·3322	109	2·26	−0·18	31
10	9-*p*-Tolyloctadecane	345	12·63	0·3372	135	2·5	+0·12	34

The number of rings per molecule calculated by this procedure are in poor agreement with theoretical values. The last column in the table refers to the percentage of aromatic carbon atoms per molecule, A, calculated by the following equation proposed by Deanesly and Carleton :—

$$A = \frac{1191 \cdot 5h}{100 - y}$$

The values obtained in the above cases are about 10 units higher than theoretical weight per cent carbon atoms in aromatic rings. The authors also tried to extend their method to oils containing olefins, the unsaturation due to olefins being determined by the bromine number method. No data on the reliability of this method when applied to pure hydrocarbons are available.

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INTERIM REPORT OF THE OXIDATION PANEL.

The following appendixes were inadvertently omitted from this report when published in the June issue (pp. 336–44) of the Journal.

APPENDIX IV.

RESULTS OBTAINED WITH THE MODIFIED SUNBURY BEAKER-CORROSION TEST.

Oil ref. no.	1.	2.	3.	4.	8.	5.	6.	7.	9.
Type.	H.D.	H.D.	H.D.	H.D.	H.D.	Mineral.	Mineral.	Mineral.	Detergent.
Laboratory A.									
Test 1	10	4	2	4	6	468	365	228	647
Test 2	9	5	3	4	7	437	358	260	694
Average	10	5	3	4	7	453	362	244	671
Order of merit	5	3	1	2	4	8	7	6	9
Laboratory B.									
Test 1	10	15	10	8	15	539	390	240	825
Test 2	17	21	8	14	7	462	310	208	806
Test 3	—	—	—	—	—	324	—	—	—
Average	14	18	9	11	11	442	350	224	816
Order of merit	4	5	1	2=	2=	8	7	6	9
Laboratory C.									
Test 1	8	7	5	2	5	395	292	299	457
Test 2	6	5	7	14	4	406	278	254	544
Average	7	6	6	8	5	401	285	277	501
Order of merit	4	2=	2=	5	1	8	7	6	9
Laboratory D.									
Test 1	7	20	17	18	6	310	333	333	491
Test 2	10	7	6	8	6	468	249	119	571
Average	9	14	12	13	6	389	291	226	531
Order of merit	2	5	3	4	1	8	7	6	9
Laboratory E.									
Test 1	5	10	4	2	2	617	454	363	797
Test 2	3	6	2	1	2	652	466	358	772
Average	4	8	3	2	2	635	460	361	785
Order of merit	4	5	3	1=	1=	8	7	6	9
Laboratory F.									
Test 1	2	7	2	1	1	376	350	564	545
Test 2	3	5	1	1	1	363	338	522	606
Test 3	—	—	1	—	—	—	374	—	—
Average	3	6	1	1	1	370	354	543	576
Order of merit	4	5	3	1=	1=	7	6	8	9
Summary.									
Lowest, mg.	3	5	1	1	1	370	285	224	501
Variation, %	−63	−50	−83	−86	−80	−17	−19	−28	−23
Mean, mg.	8	10	6	7	5	448	350	313	647
Highest, mg.	14	18	12	13	11	635	460	543	816
Variation, %	+75	+80	+100	+86	+120	+42	+31	+74	+26
Spread, mg.	11	13	11	12	10	265	175	319	315
Spread, %	138	130	183	172	200	59	50	102	49
Reproducibility, ±%	69	65	92	86	100	30	25	51	25

APPENDIX V.

Modified Indiana Oxidation Corrosion Test.

Development and Test Procedure.

The test procedure is based upon the Indiana stirring corrosion test.

Much development work has been conducted by the co-operating laboratories, and this has followed two lines :—

Modifications in the apparatus.
Modifications in the test procedure.

In the first category, attention has been given to the fixing of the test piece and catalyst and to the design of the stirrer, whilst in the second various running periods and periods between change of test piece and catalyst have been examined, with a view to obtaining a clear-cut distinction between straight mineral oils and approved H.D. oils, on the basis of corrosion and oxidation.

The method comprises stirring a measured quantity of the oil at 160° C with a stainless-steel stirrer in the presence of a test piece of pure lead and a copper catalyst.

Corrosion is assessed by determining the cumulative loss in weight of the lead test pieces after a 12-hour period and the degree of oxidation by estimating the acidity, and the viscosity increase at 100° F after an 18-hour period.

The apparatus and test procedure has so far been standardized as follows :—

Apparatus (Fig. 4).*

This shall consist of a Pyrex glass beaker and a stainless-steel stirrer (Fig. 5) † together with means of suspending the test piece and catalyst. A heating bath shall be provided for maintaining the oil in the beakers at 160° ± 1° C.

(a) *Beakers.*—400-ml Pyrex, tall form, without lip as specified in M.O.S. Spec. CS. 2091.

(b) *Thermometers.*—S.T.P.T.C. T.9a.

(c) *Heating Bath.*—To allow the immersion of the beakers so that the oil level in the bath is the same as in the beakers when the latter is at a temperature of 160° C, and the oil is being stirred. The top of the beaker to be level with the top of the bath, which shall be fitted with a metal screen 6 inches high.

(d) *Stirrer and Shaft.*—To be of stainless steel throughout, to the design shown in Fig. 5 the bottom of the stirrer to be 3 mm from the bottom of the bath and the top of the shaft to be fitted with a suitable arrangement for mechanical stirring at a constant speed (Fig. 6).‡

(e) *Test Pieces.*—These shall be 3 cm × 1 cm × 0·5–1·0 mm thick, prepared from chemical lead Type A to B.S.S. 334–1934, and held rigidly in the oil stream with a glass support 9 cm below the top of the beaker and 1 cm from the side (Fig. 7).§

(f) *Catalysts.*—These shall be 3 cm × 1 cm, cut from pure electrolytic soft copper sheet 0·1 mm thick, and shall be suspended in a manner similar to that described for the test pieces but on the opposite side of the beaker.

Procedure.

(a) *Preparation of Test Piece.*—Surfaces shall be prepared first by lightly scraping if this is necessary and then by use of Russell's solution. The test piece shall be dipped into this solution for 1 minute, after which the resulting brown stain shall be washed off in running water. This etching procedure shall be repeated three times to give a bright crystalline surface. The test piece shall be finally rinsed with distilled water, dried between filter-papers, and then stored under dry I.P. spirit before and after weighing until required for use. Russell's solution shall be prepared for immediate use by mixing equal quantities of two solutions, the first consisting of 45 g of ammonium molybdate in 300 ml of water and the second of 80 ml concentrated nitric acid in 220 ml of water, stirring until the resulting precipitate has dissolved.

(b) *Preparation of Catalyst.*—Surfaces shall be prepared in accordance with the method described in I.P. 56/46, Section 4 (*d*).

(c) *Assembly.*—200 ml at 15° C of the oil to be tested shall be weighed into the beaker. When the oil-bath has reached a temperature sufficient to maintain the oil under test at 160° ± 1° C, the beaker shall be placed in position with the thermometer arranged so that the bottom of the bulb is 2·5 cm above the bottom of the beaker.

(d) *Method.*—The beaker shall be preheated in the oil-bath for half an hour before

* See page 341. † See page 342. ‡ See page 343. § See page 344.

the test is commenced. During the last 10 minutes of this period the weighed test piece and catalyst shall be introduced. Stirring at 1100 ± 40 r.p.m. shall then be commenced and continued for 3 hours when the test piece and catalyst shall be changed during a 10-minute interval. The test is then continued for a further 15 hours, changing the test piece and catalyst every 3 hours during a 10-minute interval. If it is more convenient, the test may be carried out in three periods of 6 hours on consecutive days, the beakers being removed from the bath at the end of each such period.

Assessment of Corrosive Effect.—As soon as possible after the test pieces have been removed from the beaker they shall be freed from oil and any loose material by washing with benzene, and by lightly brushing with a camel-hair brush wetted with this solvent. They shall then be dried and weighed. The sum of the losses in weight of the first four test pieces constituting one test expressed in milligrams shall be recorded.

Assessment of Oxidation.—The oil remaining in the beaker at the end of the 18 hours shall be tested for acidity (I.P. 1/46 Method A), and viscosity increase at 100° F, and the results recorded.

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Geology.

1986. Stratigraphic convergence problems. R. R. Wheeler and R. M. Swesnik. *World Oil*, Apr. 1950, **130** (5), 57.—Stratigraphical traps are classified, and the genetic approach to their interpretation is emphasized.

Stratigraphical traps can be placed in two groups: (1) due to convergence of bedding planes because of truncation, onlay, or offlap; (2) due to variation in porosity as a result of facies change between bedding planes. Stratigraphic convergence is always associated with a plane of unconformity. Convergence formulæ can be derived by algebraically stating the relationship of the converging dip of beds above and below the unconformity. Examples are given.

Cross-sections to illustrate the various types of trap are included. C. A. F.

1987. Whence the oil of the Athabaska tar sands? M. Y. Williams. *Trans. Roy. Soc. Canada*, June 1949, **43**, Ser. 3, 149.—The history of the discovery and the theories of the origin of the Athabaska tar sands are summarized.

Adequate sources in Mesozoic formations are remote, and lateral migration presents difficulties. It is probable that the oil in the tar sands has been derived from underlying Middle Devonian limestones. C. A. F.

1988. Photogeology's place in petroleum exploration. L. Brundall and A. R. Wasem. *World Petrol.*, Mar. 1950, **21** (3), 51; Apr. 1950, **21** (3), 41.—The principles of photogeology are briefly described, with reference to types of photographs, flying area, scale, sources of maps and charts, stereoscopy, dip estimation, and photogeological symbols, field checks, structure contour maps, completion procedure, etc. Examples are given. G. D. H.

1989. Photogeology applied to petroleum exploration. A. R. Wasem. *World Oil*, Apr. 1950, **130** (5), 64.—Photogeology is widely used as an aid in oil exploration, particularly in reconnaissance or in the solution of special problems in surface mapping. Use of the techniques involved saves considerable time and money.

The methods and techniques used in the preparation of geological and structural contour maps from aerial photos are discussed, and examples are given. C. A. F.

1990. Thermal analysis of clay minerals. J. J. Glogoczowski. *Nafta*, June 1949, **5**, 141–3.—Thermal analysis is used to determine points of loss of water, decomposition, crystallization, and recrystallization. Methods in use are described and some results are plotted. Uniform rate of temp increase must be preserved. Automatic recording on a strip shows that mixtures of minerals show characteristics of all their constituents. Percentage composition can in this fashion be easily determined. M. S.

1991. The age of "Godulka"-rocks and "Węglówka"-limestones (marls).—J. Czernikowski. *Nafta*, May 1949, **5**, 111–12.—Author deals with errors made by authors who have previously tried to determine the age of these rocks. Using micropaleontological data new conclusions are reached by the author. M. S.

1992. Bacterial activities and the origin of oil. C. E. Zobell. *Petroleum*, May 1950, **13** (5), 109–11.—Assuming that oil has had an organic origin it is certain that bacteria and allied micro-organisms have contributed to the formation of petroleum. It is apparent that bacteria could live and may be biochemically active in nearly any environment where petroleum occurs in nature. Living bacteria have been detected in petroliferous sediments and reservoir fluids.

The action of bacteria upon organic matter is discussed. Laboratory and field observations indicate that under certain conditions bacteria tend to convert organic matter into petroleum-like residues. During and after its formation, the oil may be modified in various ways by bacteria which attack hydrocarbons and other constituents

of petroleum. Bacteria may also liberate oil from oil-bearing materials, and may have made a significant contribution to the migration and accumulation of oil.

R. E. P.

1993. Oilfield fossils of the paleocene system. D. T. Setterington. *Petroleum*, Mar. 1950, **13** (3), 66–7.—Describes typical oilfield fossils of the Paleocene era that came at the beginning of Tertiary times. The organisms include the lamellibranchs, gastropods, and the foraminifera, and have been most valuable in providing stratigraphical information for the petroleum industry. R. E. P.

1994. Offshore petroleum resources. V. S. Swaminathan. *Petroleum*, Jan. 1950, **13** (1), 5–7.—Offshore, submarine areas adjacent to existing producing regions will undoubtedly prove increasingly important in the near future. It is concluded that the oil resources of the Continental Shelf should be relatively larger than those of present land areas.

Details are given of drilling sites, and economic and technical problems are discussed. Wells should cost three or four times as much as similar land wells, and production costs will be high. The latter can be reduced by high field production rates and by reducing the number of wells drilled.

Oil wells sunk beneath the sea in the Gulf of Mexico are expected to produce some 25,000 brl of crude petroleum a day within the next five years. R. E. P.

1995. How deep oil and gas may be expected. J. S. Cloninger. *World Oil*, May 1950, **130** (6), 57.—The max depth at which oil and gas may be expected is governed by three factors: the depth to which pores, fractures, cavities, and other openings may exist in sedimentary rocks; the depth to which favourable sedimentary rocks such as unaltered sandstone, shale, and limestone can be expected; the depth to which oil or gas can be expected to exist if favourable sedimentary rocks are present.

Theoretically oil or gas may occur in sandstones down to 65,620 ft and in limestones to 51,300 ft. Thus it would be possible, if source beds were present, for oil and gas to be found near the bottom of all favourable sedimentary basins in the U.S.A., excepting the San Joaquin–Sacramento basin which has a depth of 65,000–75,000 ft.

A map showing the deep sedimentary basins in the U.S.A. is included. C. A. F.

1996. U.S. liquid hydrocarbon reserves rise 1·5 billion barrels in 1949. Anon. *World Petrol.*, Apr. 1950, **21** (4), 34.—At the end of 1949 U.S. proved reserves were estimated to be 180,000,000,000 M.c.f. of natural gas and 28,300,000,000 brl of crude oil and natural-gas liquid. The 1949 production figures were 6,008,000,000 M.c.f. of gas and 2,186,000,000 brl of crude oil and natural-gas liquids. The corresponding 1948 figures are given for comparison. G. D. H.

1997. Exploratory drilling in 1949 increased 13%. Anon. *World Petrol.*, May 1950, **21** (5), 58.—In 1949 the U.S. had 9058 exploratory wells totalling 26,438,601 ft, 1830 were producers. There were 464 successful new field wildcats based on technical advice and 3143 dry holes; the corresponding figures for wells not based on technical advice were eleven and 367.

Canada has fifty-eight producers out of 262 exploratory wells, and Mexico fourteen producers out of fifty-one exploratory wells.

Brief notes are given on important areas, and a table shows the relative success of exploratory drilling in the U.S.A. yearly from 1944. G. D. H.

1998. Recent geological developments in western Anadarko basin, Texas and Oklahoma Panhandles. G. L. Meholin. *Bull. Amer. Ass. Petrol. Geol.*, **34** (7), 1530–9.—During the past two years twelve deep (Mississippian or Ellenburger) wildcat tests have been drilled in the Texas Pandhandle part of the Anadarko basin. These have served to give some insight into the structure and deposition of this part of the basin. A few questions have been answered, and a great many more have been posed which only additional drilling can answer. E. N. T.

1999. Ringwood, Elk City focus attention on Anadarko geosyncline. J. A. Kornfeld. *World Petrol.*, June 1950, **21** (6), 34.—Elk City has fifty-two deep gas-distillate wells,

and Ringwood sixty-two oil wells. The former produces from the Hoxbar at 8800–10,200 ft on an elongated anticline with 40 ft of closure. It was discovered in 1947. Ringwood was discovered in 1945 and produces from the Manning sand stratigraphic trap. About 8000 acres are proved. The Rocky field is on the north flank of the Washita mountains. It was discovered in 1946. Southwest Dover was opened in 1948 with gas and distillate from the Hunton and Simpson. Willco 1 in Sherman County has found oil in the Pennsylvanian at 5844–5880 ft. It is on an anticline north of and parallel to the Amarillo Arch. Lips 1 found Mississippian oil production in 1949, and 1 mile to the northwest gas-distillate was obtained in the Pennsylvanian in Lips 2. On the east side of the Hugoton field in southwest Meade County, Kansas, Adams Ranch 1 found gas-distillate in the Mississippian. The Kismet oilfield is in the Hugoton embayment, and produces from the Pennsylvanian.

The findings of a number of additional wells are briefly summarized, and a series of tables present data on well completions, ownership, drilling activity, reservoir statistics, formation levels, etc., in certain cases.

The Anadarko basin is bounded by the Nemaha axis on the east, the Central Kansas uplift on the north, and includes the Texas and Oklahoma Panhandles.

The formations in it are briefly described, and maps show the oil and gas fields, the tectonic features, and the form of the basement, the Viola and the Mississippian.

G. D. H.

2000. South Canyon Creek dolomite member, a unit of phosphoria age in Maroon formation near Glenwood Springs, Colorado. N. Wood Bass and S. A. Northrop. *Bull. Amer. Ass. Petrol. Geol.*, **34** (7), 1540–51.—The South Canyon Creek dolomite member of the Maroon formation crops out at many places from South Canyon Creek, which is 4½ miles west of Glenwood Springs, Colorado, northwestward for 22 miles. The thickness of the member ranges from 1½ to 6½ ft. A preliminary study of the fossils collected from the member has yielded a tentative list of twenty-four forms, comprising nineteen pelecypods, two scaphapods, and three gastropods. The fauna appears to be a Permian one of Phosphoria age. E. N. T.

2001. Deformation of Fort Union formation near Lignite, North Dakota. R. C. Townsend. *Bull. Amer. Ass. Petrol. Geol.*, **34** (7), 1552–64.—The Fort Union formation (Paleocene) has been generally believed to be essentially horizontal in northwestern North Dakota. It is intensely folded and faulted in an area southwest of the town of Lignite, northwestern North Dakota, as shown in exposures in a topographic bench along the northeast or proximal slope of the Altamont moraine. It is suggested that the structures described may be genetically related to the bedrock high on which the Altamont moraine is deposited, and that the Fort Union formation may be folded and faulted over a wider area than is now known. Also, structures in the Fort Union formation may reflect deformation of older rocks at depth. E. N. T.

2002. Cities Service drills 6 wells in Kansas. Anon. *Petrol. Engr.*, June 1950, **22** (6), B-76.—The Hunt gas well in Seward County was completed for 12,100,000 cu. ft. gas/day.

Five oil producers were completed for a total of 2126 b.d. The largest was Lorenz 2, in the Batholemew pool, Sedgwick County, which produced 1748 b.d. C. A. F.

2003. Oil in eastern Kansas. J. M. Jewett. *World Oil*, May 1950, **130** (6), 64.—Nine wells completed in the Davis Ranch field, Wabaunsee County, eastern Kansas, had potentials ranging up to 3000 b.d. from approx 3200 ft. 50,000 brl from the field were marketed in 1949. Production is from Ordovician Viola limestone, which is folded in a broad synclinal belt east of the Nemaha Uplift in the deepest part of the Forest City basin.

Thirty-seven wildcats subsequently drilled in the neighbourhood of the Davis Ranch field were dry, but nevertheless it is believed that further pools similar to the Davis Ranch field will be discovered in the general area. Detailed surface mapping, core-drilling, and geophysical work are in progress. The western portion of the Kansas sector of the Forest City basin is expected to be very active in the near future.

Hitherto production in eastern Kansas has chiefly been from shallow Pennsylvanian

sheet and shoestring sands. Half the current production is obtained by water-flooding these sands.

Oil has been found in the Ordovician in forty-seven fields, chiefly close to unconformities below the Pennsylvanian, Chatanooga shale or Mississippian limestone, Maquoketa shale, and in the St Peter (Simpson) sandstone. In many areas of prolific Pennsylvanian production, the underlying Ordovician has been inadequately tested.

Forty-three references are given. C. A. F.

2004. New production found in Louisiana Parish. Anon. *Petrol. Engr*, June 1950, **22** (6), B-81.—1 V. J. Kurzweg *et al*, 2½ miles southwest of the Lottie field, Pointe Coupee Parish, flowed 9,424,000 cu. ft. gas/day and 336 b.d. of condensate from 10,324 to 10,330 ft. C. A. F.

2005. Mississippi structures and their relation to oil accumulation. E. P. Thomas. *Bull. Amer. Ass. Petrol. Geol.*, **34** (7), 1502–16.—An intensive search for oil in Mississippi during the past decade has provided considerable information regarding local structures. All the known fields are found either in structural or combination structural and stratigraphic traps. The producing structures may be divided conveniently into four groups: (1) igneous intrusions, (2) piercement salt domes, (3) deep-seated salt domes, and (4) normal faults and grabens. A discussion of the general features, distribution, petroleum production, origin, and geologic history of each group is given. E. N. T.

2006. Brookhaven oilfield, Lincoln County, Mississippi. R. Womack, Jr. *Bull. Amer. Ass. Petrol. Geol.*, **34** (7), 1517–29.—The Brookhaven oilfield is in the central part of the interior salt basin of Mississippi and was discovered in 1943. The Brookhaven structure is anticlinal, and is probably due to deep-seated salt movement. The structure is crossed by three normal faults which form a central graben area. Oil is produced from depths ranging from 10,135 to 10,545 ft from the Tuscaloosa formation of Upper Cretaceous age. Accumulation is controlled by structure and the lenticularity of the producing sands. E. N. T.

2007. Discovery and development of crude oil and gas reserves in Cheyenne County, Nebraska. W. L. Hershelman. *Petrol. Engr*, June 1950, **22** (6), B-50.—Mary Egging 1, in Cheyenne County, Nebraska, found pay at approx 4400 ft in 1949. Subsequent wells in the area developed the Huntsman and Gurley fields, confirming that oil exists in productive quantities in the Julesburg basin.

Surface formations in Cheyenne County are easterly dipping Tertiary beds reaching 1000 ft in thickness, and overlying westerly dipping Cretaceous sands, shales, and limestones. Pay zones at Gurley and Huntsman are Cretaceous " Dakota " sands.

For many years the Cretaceous shale sequence was known to be petroliferous, and potential reservoir rocks, such as the Muddy, Dakota, and Lakota sands were known. A seismic programme was started in 1943, and a number of subsequent wells drilled on features of small structural closure were dry. A second exploration phase since 1946 has found structural conditions in Cheyenne County to be favourable for oil accumulation.

The Gurley field has over 100 ft of closure. Ten wells have been drilled, and one is drilling. Of these, seven are producers and three are dry. Production is chiefly from the first bench of the " so-called " Dakota. Wells average 100 b.d. of 35° oil on pump.

The Huntsman structure, 8 miles southwest of Gurley has also over 100 ft of closure. The discovery well, 1 Cruise, made 54 M.c.f. gas/day. Oil is present in the Dakota first and third benches.

The discovery of further substantial reserves in the Julesburg basin is expected. C. A. F.

2008. Magnolia well finds new Devonian area. Anon. *Petrol. Engr*, June 1950, **22** (6), B-82.—1 Lightcap Land Co., in Chaves County, New Mexico, produced 146 brl of 52° oil in 2¼ hr. G.O.R. was 1527 : 1. Pay was topped at 7970 ft. C. A. F.

2009. Wilcox brings in producer. Anon. *Petrol. Engr*, June 1950, **22** (6), B-76.—1 Dugger, Beckham County, Oklahoma, found oil and gas between 10,950 and 11,050 ft. The well is 6 miles west of the Elk City field, and the pay is believed to be equivalent to the productive zone at Elk City. C. A. F.

2010. Greenbrier opens new pool. Anon. *Petrol. Engr*, June 1950, **22** (6), B-82.—1 Wentzell, in McClain County, Oklahoma, on a test of the Bromide sand from 10,668–10,693 ft, flowed 39·6° oil at a rate of 40–50 brl/hr. C. A. F.

2011. Makes Clay County strike. Anon. *Petrol. Engr*, June 1950, **22** (6), B-82.—1 Tate, in Clay County, Texas, on completion flowed a calc potential of 1203·84 b.d. of 43° oil from the Strawn sand. The well is 3 miles northeast of the Chapman Strawn pool. C. A. F.

2012. Major discovery made in Hockley County. Anon. *Petrol. Engr*, June 1950, **22** (6), B-82.—1 Underwood, 4 miles south of Smyer, Hockley County, West Texas, on test flowed 41° oil at a rate of 75–150 brl/hr. Canyon reef pay was topped at 9285 ft. C. A. F.

2013. Scurry County stimulates search for reefs. W. M. Osborn. *World Oil*, Apr. 1950, **130** (5), 40.—Estimated proved reserves of Scurry County, Texas, are 1 (U.S.) billion brl.

Discovery of the North Snyder pool in 1948 and later discoveries has emphasized the need for studying reef limestones and techniques for locating them.

Oil was discovered in the Pennsylvanian shale section in 1938, but its significance was overlooked until the post-war discoveries showed the Pennsylvanian sequence to be a major producing zone in the Permian basin area.

In the North Snyder pool, oil is produced from Pennsylvanian Canyon reef. The structure is an elongated build up tending approx 22 miles in a northeast–southwest direction. There are several major high areas along the trend, of which the North Snyder area shows the highest reef development. The limestone is chiefly crystalline, but is chalky in part. On the flanks of the structure it is broken by shale streaks. Porosity is intercrystalline to cavernous, and there is horizontal and vertical fracturing. The reef started growing during the Strawn, with greatest development in the Canyon.

The Snyder area is served by two 8-in and two 6-in pipelines. Two additional 8-in and one 6-in lines are under construction, and a further 8-in and 10-in lines are planned. Two gasoline plants are to be built.

A regional map, structural maps, and cross-sections of the Snyder area are included. C. A. F.

2014. The Diamond M reef of Scurry County Texas. E. D. Klinger. *World Petrol.*, Apr. 1950, **21** (4), 36.—The Diamond M field of southwest Scurry County lies 14 miles north of the Westbrook field of Mitchell County where the first Permian basin production was found in 1920. Subsurface data indicated a shallow structure north of the Sharon Ridge field, and in 1945 a well (No. 1 McLaughlin) was begun to explore the Permian. It was abandoned at 3724 ft. In 1946 a seismic survey was made to determine pre-Permian structure; it was concluded that Pennsylvanian reefs were present, and this was confirmed by No. 1 Schattel, several miles east of the Diamond M block in 1948. No. 2 McLaughlin found oil and gas in the Canyon reef limestone and flowed 150 brl/hr from perforations at 6592–6614 ft after acidizing. The Sharon Ridge Canyon field was discovered in 1949, but it is not known whether it is continuous with Diamond M.

At Diamond M Triassic red beds are at the surface with Permian about 700 ft deep. The Pennsylvanian is at about 6500 ft, and the Canyon is crystalline dolomitic limestone with many vugs and fractures. The Strawn has not been reached at Diamond M. The attitude of the base of the Canyon reef is not known; it may not be folded. The top of the reef varies in level, and the overlying Permian follows these variations.

The oil is 43° gravity. Little is known about the water level, which may be at 4500 ft subsea. A stratum contour map is given. G. D. H.

2015. Warren opens new area. Anon. *Petrol. Engr*, June 1950, **22** (6), B-81.—1 Cunningham, 15 miles north of Snyder, Scurry County, Texas, on test had an indicated potential of 1200 b.d. on restricted flow. Canyon reef pay was topped at 6830 ft.
C. A. F.

2016. Imperial River section, Mackenzie Mountains, Northwest Territories, Canada. L. R. Laudon. *Bull. Amer. Ass. Petrol. Geol.*, **34** (7), 1565–77.—The details of an excellently exposed section in the Imperial River Canyon, Mackenzie Mountains, Northwest Territories, Canada, involving Cambrian, Silurian, and Devonian rocks are presented. Two Cambrian formations, Macdougal at the base and an unnamed formation at the top, two Silurian formations, the Ronning followed by the Bear Rock, and three Devonian formations, Ramparts, Fort Creek, and Imperial are recognized. Cyclic units are recognized throughout much of the section. E. N. T.

2017. Drills fourth Imperial Golden Spike well. Anon. *Petrol. Engr*, June 1950, **22** (6), B-78.—A well north of Shoepp 1 in the Canadian Golden Spike field, on test flowed oil to surface in 22 min and blew gas at a rate of 400,000 cu. ft/day, from 5919–5970 ft.
C. A. F.

2018. Makes Argentina find. Anon. *Petrol. Engr*, June 1950, **22** (6), B-78.—A new pay has been discovered at 7500 ft in the Punta Piedras field of Comodoro Rivadavia, Argentina. Production from the discovery well is said to be 150,000 litres/day.
C. A. F.

2019. Cuba's oil outlook. J. E. Kastrop. *World Oil*, May 1950, **130** (6), 219.—Recent intensive field investigations in Cuba have indicated the possibility of source beds and reservoir rocks in the sedimentary formations in the southern part of the island and on the coastal shelves. A well drilled 2 miles offshore in Cardenas Bay is said to have found oil and gas.

Subsurface geology is very complex, and chiefly consists of north–south gravity faulting and tilting on older east–west trending folds and thrusts. There are several broad domes, and some anticlines are closed. Sedimentary formations range from pre-Jurassic metamorphics to Recent, and there are intrusives and extrusives. Several Jurassic, Cretaceous, Eocene, and Oligocene beds are possible source rocks, and there may be good reservoir rocks in the Cretaceous, Miocene, and fractured igneous masses. Oil and gas seeps and asphalt deposits have been found in the most eroded and disturbed parts of the island. Little exploratory work has been done in the least-disturbed area in the western and eastern coastal plains, and in the southern shallow submarine shelves and related basins.

Cuban demand for oil is about 35,000 b.d. The island's production is probably less than 500 b.d. 1949 estimated production from the Motembo, Bacuranao, and Jarahueca fields was 172,400 brl. Motembo and Bacuranao are producing insignificant amounts.

The economic and labour problems of oilfield development in Cuba are discussed.

A tectonic map and structural cross-sections are included. C. A. F.

2020. New oil field discovered in France. Anon. *Petrol. Engr*, June 1950, **22** (6), A-40.—A new oilfield has been discovered in France, about 15 miles northwest of Pau near the Pyrenees. Surface beds are Pleistocene with no indication of structure. Seismic work outlined an anticline trending northwest–southeast. Total closure on the structure is 900 ft, with good closure on the northeast flank. The southwest flank is complicated by faulting.

The discovery, Lacq 1, drilled in 1949, found saturated Cretaceous limestone and dolomite at 2289 ft. On completion the well flowed 20 b.d., but later, on pump, production increased to 140 b.d. A second well about 170 ft northeast of Lacq 1, completed in April 1950, produced 9000 b.d. on 1¼-in. choke.

Additional wells are being drilled. C. A. F.

2021. Exploratory drilling planned in North Holland this year. Anon. *World Oil*, May 1950, **130** (6), 240.—Exploratory drilling is to be carried out in the Zaan region and

at Warmenhuizen in north Holland. It is reported that equipment capable of drilling to 10,000 ft will be used. C. A. F.

2022. Spain stepping up its search for oil. H. S. Williamson. *World Petrol.*, Apr. 1950, **21** (4), 48.—Oil seeps occur at many points in Spain, and oil traces have been found in water wells. Modern methods of search for oil are being introduced. At Villanueva de Rampalay, about 75 km south of Santander three wells under 3000 ft deep have been sunk and over 300 brl of oil collected. A 7622-ft dry hole was drilled in Lerida near the French border. A well near Burgo de Osma in Soria province has reached 7253 ft. Showings at 200 ft were found in a well near Chiclana in Cadiz.

Gas and small oil showings are known in Spanish Morocco. G. D. H.

2023. 1949—a successful year for exploration in Germany. Anon. *World Oil*, Apr. 1950, **130** (5), 239.—Discoveries in Germany in 1949 increased the country's total estimated reserves from 14 million tons to 36 million tons, and output in 1949 was 32·4% higher than in 1948.

New fields were explored and two deep productive anticlines (Suderbruch and Eldingen) were found in the Hanover area, where until recently oil has been produced only from salt domes. The Scheerhorn wildcat discovered the first stratigraphical trap in Germany. Wildcatting is planned in Muensterland, and exploration wells are to be drilled in the foreland of the Swabian–Bavarian Alps, where geophysical surveys are in progress. The underground structure of Cuxhaven on the North Sea coast is to be proved. Approx 162 rigs are operating in Western Germany. 392 wells were drilled in 1949, of which only 37% were unsuccessful.

Exploration, drilling, and the new pools in Western Germany are described. A map shows the location of the fields. C. A. F.

2024. Czechoslovakia has discovery. Anon. *World Oil*, May 1950, **130** (6), 240.—The discovery of oil has been reported near Malacky, Slovakia. It is said that Russian authorities believe the occurrences to be an extension of the important Austrian fields near Zisterdorf. C. A. F.

2025. Greek crude oil from Zante Island. E. Bobos. *Petroleum*, Jan. 1950, **13** (1), 14–15.—It is probable that the total quantity of oil produced from the Keri area up to date exceeds 5000 tons even though no systematic exploitation has been made.

The black, viscous oils have a high sp. gr., are poor in light fractions, but contain reasonable quantities of kerosine fractions and are exceptionally rich in lubricants. They also contain relatively large amounts of asphalt and sulphur, although not markedly inferior to some Venezuelan oils. Tables give the first complete results to be published for the laboratory examination of the oil.

Most of the oil is refined on the island itself. Gas oils, light and heavy diesel oils, and various types of lubricating oils have been produced.

The oil would be suitable for cracking, but before erecting a plant the presence of reasonably large quantities of oil must be confirmed. R. E. P.

2026. U.S. firms to enter Tunisia. H. Ozanne. *World Oil*, May 1950, **130** (6), 228.—American operators are to make seismic and magnetometer surveys in Tunisia. Previous drilling in the country has been shallow and infrequent. A wildcat drilled at El Haroun was abandoned at 9500 ft.

The structure of northern Tunisia consists chiefly of complicated folds with salt and gypsum intrusions. In the centre of the area there are elongated anticlines. The sedimentary sequence is thick and ranges from Trias to Recent. Marine Tertiary is not present in southern Tunisia, but marine Cretaceous is well developed in the central area. C. A. F.

2027. Qatar to add 150 million barrels to Middle East production in 1950. Anon. *World Petrol.*, Mar. 1950, **21** (3), 62.—Commercial production from Dukhan on the Qatar Peninsula began at the end of 1949. The output during 1950 is expected to average 40,000 b.d. The field was discovered in 1940, by a 5000-brl well and production is from the Jurassic Zekrit formation, which consists of limestones interbedded

with anhydrite at depths of more than 5000 ft. The surface anticline is 50 miles long, 5 miles wide, with 300 ft of closure.

Drilling and living conditions are briefly described. G. D. H.

2028. Occurrence of fossil resins in the oil-shales of the Punjab Saline series. S. R. Narayana Rao. *Nature*, 1950, **165**, 654.—Since resin-bearing plants are unknown from strata other than carboniferous the presence of fossil resin in oil shales of the Saline series renders untenable a suggestion that the oil shales are of Cambrian age. Oil shales from the Chittidil region show numerous resin bodies of about 1 cm length, transparent and golden-yellow, and lying parallel with each other and with the laminations of the shale. The resins contain decomposed plant tissues but no recognizable organic remains.

The pre-Cambrian coal interbedded with the Vindhyan limestones is algal in nature and does not seem to be derived from vascular plants as with the Punjab oil shales. The Vindhyan coal and the Punjab oil shales are therefore derived from totally different types of vegetation, and there is no evidence to suggest that the two are contemporaneous. H. C. E.

2029. Shell begins drilling for oil in Queensland. Anon. *Petrol. Engr*, June 1950, **22** (6), B-63.—A deep test has been started at Morella, 100 miles south of Springsure, Queensland, Australia.

Search for oil in 1940 has involved surveys of large areas of central and western Queensland. Much of the area has been air photographed. C. A. F.

Geophysics and Geochemical Prospecting.

2030. Locating oil fields with radio waves. W. M. Barrett. *World Petrol.*, Mar. 1950, **21** (3), 46.—Radio waves are fed into the earth through a special directive radiating system, and a portable receiver picks up these waves. The transmitter is at one end of a traverse, and the receiver is placed at successive points along the traverse. Part of the energy travels along the ground to the receiver, and part is refracted down into the earth. In the absence of an oilfield the receiver readings are determined largely by the strength of the waves travelling along the ground, and the strength declines as the distance between transmitter and receiver increases. When an oilfield is present suitable relations of the field, transmitter, and receiver cause some of the waves refracted into the ground to strike the outer boundaries of the field with partial reflection and diffraction back to the receiver, thereby giving a diagnostic anomaly. For each oil depth there is an optimum spread, and rough depth predictions become possible.

A series of examples are described. At present the method is more suited for detail surveys than for reconnaissance. It is stated to detect oil, and is therefore applied in assessing the prospects of features located by conventional geological and geophysical methods, and for finding field limits. Three to six weeks may be needed in the case of a wildcat prospect. Some 300 surveys have been made, and oil deposits at 300–9000 ft have been delineated. G. D. H.

2031. Radar as a survey instrument. O. E. Haley. *World Petrol.*, Mar. 1950, **21** (3), 48.—Radar is of value in offshore geophysical work, and it may be of use in working extensive land areas with difficult terrain or few outstanding landmarks. Azimuth determinations by most radar outfits are not sufficiently accurate for surveying. Distance measurements can be made with great accuracy and negligible trouble arising from refraction. 20-ft accuracy is practicable and permits readings to be made in 10 sec.

Triangulation technique is employed using suitable targets on and off shore, after calibrating the equipment. Surveyed lines are marked by expendible marker buoys, and then the seismic work is executed.

Duct effects in the atmosphere of certain areas and particularly at certain seasons may permit detection of surface targets at distances up to 50 miles. These effects disappear in wind, rain, and fog. G. D. H.

2032. Seismograph prospecting on the Continental shelves. J. L. Soske. *Petroleum*, Feb. 1950, **13** (2), 31–5.—Describes some of the techniques and instruments which are

being used. Offshore seismic operations are more elaborate but are basically similar to those on land. Operations on water lend themselves to high speed and large production.

Seismic waves are transmitted through water, the seismometers being suspended anywhere in the water or placed on the solid bottom. Recording instruments are usually installed aboard the boat used to drag the cable system to which the seismometers are attached. Shots are fired at frequent intervals, and surveying is rapid and relatively simple.

Radar and associated radio navigation aids have been applied for the purpose of locating the exact geographic position of offshore operations.

Ammonium nitrate is used as the explosive because large quantities of it can be taken aboard ship without the presence of the danger hazard usually associated with regular highly explosive dynamites. R. E. P.

2033. Prospecting for reefs with the seismograph. E. D. Alcock. *World Oil*, Apr. 1950, **130** (5), 74.—Seismic surveys have contributed to the discovery of productive reef limestones in Texas and Canada in recent years.

Only rarely has it been possible to obtain reflections from the top of the reef. Structures in beds overlying reefs caused by differential compaction can be detected by the seismograph, provided that the relief exceeds the resolving power of the seismic method.

Reefs may also be detected by their differential velocity characteristics. In areas where the reef has a materially higher velocity than the surrounding sediments, a reflection is mapped which is deeper than the reef. This higher velocity causes a shorter travel time for the seismic energy, and a shallower depth will be computed under the reef than actually exists. A false " high " will then be mapped.

C. A. F.

2034. (Polish) exploratory drilling in 1948. J. Wdowiarz. *Nafta*, May 1949, **5**, 109–10.—A list of field and laboratory work done by the state company, Exploratory Drilling, throughout Poland is provided. Geophysical research by various methods gave good results, and in some cases threw a new light on known facts. Theoretical and practical advantages gained are great. M. S.

2035. (Contributory) factors (for determination) of relative productivity of oil fields. A. Kislow. *Nafta*, June 1949, **5**, 161–2 (*from* Prof. S. F. Fedorev, *Trudy, Gubinka Petr. Inst., Moscow*, 1940).—After the period of purely empirical exploration several known facts gave rise to incomplete theories. Tectonics, lithology, chemistry of underground waters, and chemistry of bituminous deposits (regenerative power $= rH$) as well as escape of gases indicate the location of new deposits. Prof. S. F. Fedorov analysed them critically. M. S.

Drilling.

2036. The micro-log. Anon. *World Petrol*, Apr. 1950, **21** (4), 40.—Micro-logging gives details of permeable and impermeable beds, especially in shale and limestone sequences where the resistivities of compact beds are over thirty times the mud resistivity. Sharp depressions in the micro-logs may be almost certain indications of caving. The electrode spacing is small, and two different spacings are used simultaneously on a pad pressed against the filter-cake on the well wall.

G. D. H.

2037. Squeeze cementing operations. G. C. Howard and C. R. Frost. *Petrol. Tech.*, Feb. 1950, **2** (2), *A.I.M.E.E. Tech. Paper No.* 2795, 53–64.—A series of tests relating to squeeze cementing have been made on shallow wells and on normal deep wells. In the former cases it was possible by excavation to see the results, and it was found that formations break down along existing zones of weakness and the cement slurry enters these as a pancake. In squeezing through perforations the slurry is most likely to enter those perforations adjacent to or communicating with zones of weakness. In open holes squeezed cement spreads laterally through about 360°; squeezing through perforations is erratic, the spread ranging 45° to 270° per perforation. When

water will not damage the formation it is preferable to mud for breakdown, and there is better subsequent sealing of perforations with cement and adhesion of cement to the formation.

Field tests indicate that the slow pumping technique gives better results and uses less cement in reaching the high final pressure. Although the latter seems to aid in giving successful cement jobs, its attainment does not necessarily mean that all perforations are plugged. Drillable and retrievable retainers seem to give similar results. Waiting on cement setting for 24 hr seems ample, and there are indications that a shorter period may be sufficient. In testing for success the differential pressure across the perforations should not exceed that expected during production.

A mixture of hydrochloric and hydrofluoric acids seems to be a better breakdown agent than either mud or water. G. D. H.

2038. Ability of drilling mud to lift bit cuttings. H. N. Hall, H. Thompson, and F. Nuss. *J. Petrol. Tech.*, Feb. 1950, **2** (2), *A.I.M.M.E. Tech. Paper No.* 2782, 35–46.—Laboratory and field experiments have been carried out on the slip of drill cuttings in the course of mud circulation in a well. In the laboratory work the relationships for flat and spherical particles differed markedly when the coeff of friction was plotted against the Reynolds number. The field test data with flat particles agreed generally with those for laboratory tests, but there was more spread. Slip velocities computed from turbulent slip equations were within $\pm$ 15% of the slip velocity values measured under field conditions.

Turbulence due to restrictions, vibrations, and rotations may change the cutting paths, giving errors in prediction of travel times.

Empirical equations have been derived, and these show that the slip velocity is dependent on cutting size and shape, mud flow constants, and flow states in the mud. The relationship between mud velocity and particle rise velocity is shown for laminar and turbulent slip, and the design of mud systems is discussed. Thus the most efficient pump speed for max cutting carrying capacity may be estimated.

G. D. H.

Production.

2039. Gas lifting in the Turner Valley field. S. F. Shaw. *J. Inst. Petrol.*, 1950, **36**, 382–6.—Some details of production in the Turner Valley field are given. Gas-lift operations are being carried out, and some results of its application are given.

A. R. W. B.

2040. Relative permeability to gas. W. J. Leas, L. H. Jenks, and C. D. Russel, *Petrol. Tech.*, Mar. 1950, **2** (3), *A.I.M.M.E. Tech. Paper No.* 2810, 65–72.—In the relative-permeability cell employed the lower face of the core is in contact with a fine ceramic disc from the lower surface of which a tube leads to a U-tube charged with mercury. By charging the tube with the liquid which saturates the ceramic disc and is also in the core it is possible by capillary pressure methods to vary the liquid saturation in the core. Means are provided for passing gas into and out of the core, with grooves on the top cover-plate and on the upper side of the ceramic disc to permit good use of the end faces for gas entry and exit. The apparatus permits the fluid saturation to be adjusted and gas-permeability measurements to be made at each saturation.

The relative permeabilities measured were consistent and reproducible. The rate of gas flow was found to have no effect on relative permeability to gas in this stationary liquid method. No definite correlation was found between specific permeability and relative permeability to gas in the systems studied. The capillary pressure curves obtained in this cell agreed closely with those obtained in a conventional displacement cell. No definite correlation was found between petrofabric features and relative permeability to gas.

Natural and artificial cores were studied. G. D. H.

2041. Inflow to incomplete wells during simultaneous existence of various filtration conditions in the stratum. I. A. Charnui. *Izvest. Akad. Nauk S.S.S.R., Otdel. Tekh Nauk*, 1950, 801–18.—A mathematical analysis. Method is given for calculating inflow to incomplete wells, which enables an indicator curve, relating outflow to

depression, to be constructed, taking into account deviations from Darcy's law in the proximity of the well side and depending on the type of filter. This method may likewise be applied in assessing actual indicator curves with the object of extrapolating them and determining the parameters of the stratum and the well. (Author's summary.) V. B.

2042. The presence of conductive solids in reservoir rocks as a factor in electric log interpretation. H. W. Patnode and M. R. K. Wyllie, *Petrol. Tech.*, Feb. 1950, **2** (2), *A.I.M.M.E. Tech. Paper No.* 2797, 47–52.—The formation factor is the ratio of the 100% brine-saturated rock resistivity to the brine resistivity. This will be a constant for a given rock irrespective of the brine only when the rock itself is non-conductive. In using electric log data the formation factor has been derived from the mud-filtrate-invaded zone resistivity and the mud-filtrate resistivity.

In experimental work to examine the effects of rock conductivity sandstone cores mounted in lucite have been set between conducting end plates and the resistivity has been measured when the pores were fully charged with various solutions introduced by a pump. In the case of a Berea sandstone the formation factor was dependent on brine resistivity, indicating that the core material was in part conductive. The conductivity of the solids was essentially constant. The true formation factor is dependent on rock texture, and the apparent formation factor approaches most closely to it when the saturating fluid is of low resistivity.

The Stevens sandstone is high in clay content and it gave similar results, but the resistivity of the solid was 35·7 ohm-metres, compared with 250 ohm-metres for the Berea sandstone and 2230 ohm-metres for Nichols Buff sandstone; the solid resistivity for alundum cores was infinite, and the formation factor was constant irrespective of the solution.

Further experiments employed slurries of commercial fullers' earth and powdered silica, the former being conductive when wet. A linear relationship was found between the amount of solids and the conductivity of the solid phase.

The resistivity of the formation cannot exceed the resistivity of the conducting solid matter in the rock. The presence of conductive solids causes the resistivity index–saturation relationship to suggest varying values of n in $R.I = \frac{1}{S_w^n}$. G. D. H.

2043. Performance characteristics of a volumetric condensate reservoir. F. H. Allen and R. P. Roe. *Petrol. Tech.*, Mar. 1950, **2** (3), *A.I.M.M.E. Tech. Paper No.* 2708, 83–90.—The theoretical performance of the small Bacon Lime zone volumetric condensate reservoir in East Texas has been calculated on the basis of flash and differential vaporization. Comparison has been made with observed performance determined from companion samples obtained during the reservoir's producing life. Bottom-hole pressures and gas and condensate production data have also been utilized. Retrograde behaviour is revealed by decreasing amounts of butanes-plus in the well effluent, followed by revaporization as the pressure approaches abandonment. The low level of separator efficiency at the time this revaporization became appreciable prevented definite advantage being taken of this feature.

The principal discrepancy between the computed and observed performance is attributed to the flow of liquid condensate from the formation, with the enrichment of the well effluent throughout most of the productive life of the reservoir. G. D. H.

2044. Determining friction factors for measuring productivity of gas wells. R. V. Smith. *Petrol. Tech.*, Mar. 1950, **2** (3), *A.I.M.M.E. Tech. Paper No.* 2777, 73–82.—Two methods are presented for calculating friction factors from flowing gas-well data. Method I is based on graphical integration of the energy-balance equation over the path of fluid expansion in the well, and requires flowing pressures and temperatures at several points. Account is taken of condensation of liquids and of wide variations in temperature and compressibility. The method is particularly good in calculating friction factors for deep high-pressure and high-temperature gas wells.

In Method II the energy-balance equation is integrated mathematically, assuming isothermal flow and constant compressibility (actually there is wide variation in temperature and compressibility in many wells). Provided that there is fair agree-

ment with the assumptions the method is convenient, and it also allows the calculation of subsurface pressure in a flowing gas well.

The accuracy of Method I is dependent on the efficiency of graphical integration. On this account the co-ordinates must be well chosen to permit good measurements of areas. G. D. H.

2045. Attainment of connate water in long cores by dynamic displacement. R. L. Slobod. *Petrol. Tech.*, Mar. 1950, **2** (3), 17–21.—Long cores have been employed in experimental studies of the efficiency of oil recovery when interstitial water is present, and generally the initial conditions have been attained by dynamic displacement from a fully water-saturated core. It is probable that in many cases the minimum interstitial water content was not reached.

Sandstone cores form outcrops of the Strawn, Torpedo, and Elgin have been investigated experimentally. The cores were 12–18 in long and 1–2 in dia. All were rather bentonitic, and one was acid-extracted before use. Brine with 50,000 p.p.m. chloride was the water phase and naphtha the oil phase. The core was in a rubber sleeve under external pressure, and in some cases provision was made for electrical-resistivity measurements of various sections. The cores were saturated after evacuating. Filtered oil was used, and when the displacing oil broke through most of the displaceable oil appeared to have been displaced. On occasions as little as three pore volumes of oil have been assumed to give the irreducible amount of interstitial water, but the present experiments indicate that 3000 volumes may, in fact, be needed. In the later stages the oil/water ratio at exit was over 20,000,000. For Torpedo sandstone six pore volumes left 34% water, 395 pore volumes 23·5%, and 1165 pore volumes 22·2%.

The above dynamic method may be useful, particularly with small core plugs.

If only a small pressure is applied to the flowing oil only a portion of the displaceable water is removed as is predicted by capillary pressure studies.

In two experiments on one core the original oil saturations were 85% and 67% (in the latter case the terminal flowing oil/water ratio was not so high as in the former, but the oil recovery was considered to be practically complete). G. D. H.

2046. The K.O.W. type of deep well pump. J. Ostaszewski. *Nafta*, Mar. 1949, **5**, 52–6.—K.O.W. pump is designed for work in depths over 2000 m, but will work just as well at lower depths. It can be extracted from the well without extracting the pipes, its more delicate parts are well protected, and the filter can be removed without removing the pump.

The paper gives sketches of the pump, its dimensions, methods of inserting and extracting it from the well, as well as possible causes of breakdowns and their removal. Productivity versus strokes per min is shown in three tables. M. S.

2047. Secondary recovery of oil by air and gas injection in the Brenneman field, Hancock County, West Virginia. E. M. Tignor and others. *U.S. Bur. Mines Rep. Invest.*, *No.* 4690, May 1950.—The Brenneman field in West Virginia was selected for a study of secondary recovery methods as being typical of the smaller reservoirs in the Appalachian area. 348 acres of the field were productive, and most of the area was developed relatively rapidly. Initial production rates reached 1000 b.d. in some wells. The field was abandoned in 1923, when production fell to 1000 brl/year, and cumulative production had reached 705,000 brl.

Secondary recovery operations were started in 1927, and peak development was reached in 1942, when ninety-two producers and twenty-six injection wells were in use. Air and air/natural gas have been used for injection. Details are given of these operations, including the equipment, measurement, and control.

It is estimated that 11·9% of the original oil in place will be produced by these secondary recovery methods. The estimated oil saturation in the reservoir at the end of economic gas injection indicates that water flooding might recover additional oil.

Details are given of the geology of the field, and structure and isopach maps and cross-sections are included. Tables give summaries of available well records and core-analysis data. Production-decline curves and development maps of the secondary recovery project are also included. C. A. F.

Oilfield Development.

2048. Completions drop in February. Anon. *World Oil*, Apr. 1950, **130** (5), 54.—2799 wells were completed in the U.S.A. in February 1950, compared with 3377 in January.

A table shows well completions in the U.S.A. in February 1950 and the cumulative for the year. C. A. F.

2049. Reserves at new highs. L. J. Logan. *World Oil*, Apr. 1950, **130** (5), 48.—Estimated reserves of liquid hydrocarbons in the U.S.A. at the end of 1949 were 28,378,501,000 brl (24,649,489,000 brl crude oil and 3,729,012,000 brl natural-gas liquids). Gas reserves were 180,381,344 M.c.f.

Tables included show: the estimated proved reserves of crude oil, natural-gas liquids, and total liquid hydrocarbons in the U.S.A., by years since 1936; a summary of changes in 1949 in proved U.S.A. reserves of crude oil, natural-gas liquids, and total liquid hydrocarbons (all oils); the estimated proved reserves of crude oil, natural-gas liquids, and total liquid hydrocarbons in the U.S.A., by states; the estimated proved recoverable reserves of natural-gas liquids in the U.S.A., by states; a summary of changes in 1949 in proved U.S.A. reserves of natural gas; and the estimated proved recoverable reserves of natural gas in the U.S.A., by states. C. A. F.

2050. Completions climb in March. Anon. *World Oil*, May 1950, **130** (6), 34.—3337 wells were completed in the U.S.A. in March 1950, compared with 3276 in March 1949. Cumulative for the year at the end of March was 9504, 7·9% greater than in 1949.

A table shows well completions in the U.S.A. for March 1950 and cumulative for the year, by states. C. A. F.

2051. Exploration leads 1949 period. C. W. Smith. *World Oil*, May 1950, **130** (6), 73.—620 exploratory wells were completed in the U.S.A. in March 1950, compared with 541 in February. 22·3% of these were successful, compared with 17·4% in February. Exploratory wells completed in the first three months of 1950 totalled 1797, 12·9% more than in the comparable period for 1949.

Tables show the results of exploratory drilling in the U.S.A. in March 1950 and the first three months 1950–1949, by districts; and the new oil, distillate, and gas fields, and new pays discovered in March 1950. C. A. F.

2052. Exploration continues brisk pace. Anon. *World Oil*, Apr. 1950, **130** (5), 92.—541 exploratory wells were completed in the U.S.A. in February 1950, compared with 636 in the preceding months. 17·4% of these were producers, compared with 20·1% in January.

A table gives results, by districts, of exploratory drilling in the U.S.A. in February 1950. C. A. F.

2053. Indiana oil production up 24 per cent in 1949. Anon. *Petrol. Engr*, June 1950, **22** (6), B-71.—9,000,734 brl were produced in Indiana in 1949. Sixty-six discoveries were made during the year, including twenty-seven new fields, fifteen extensions of old fields, and twenty-four new pays. Approx 26,000 M.c.f. gas/day open flow was discovered in 1949. C. A. F.

2054. Canada's production gained 75% in 1949. J. L. Irwin. *World Petrol.*, Mar. 1950, **21** (3), 68.—The discoveries at Leduc, Redwater, Golden Spike, Excelsior, Simmons, and Normandville since 1947 have radically altered the Canadian oil picture. In 1947 the output was 7,700,000 brl; in 1949 22,100,000 brl, with output limited to 65,000 b.d. in the second half of 1949. Canada needs a little over 60,000 b.d.

Tables give the crude-oil and natural-gas production by provinces for 1948 and 1949, and a graph of Alberta monthly oil production since 1935. G. D. H.

2055. Oil developments in Western Canada. M. L. Haider. *Canad. Min. metall. Bull.*, June 1950 (458), 321.—The history of oil discovery in Canada is described, since the first discovery of oil near Detroit in southwestern Ontario in 1861.

All fields discovered before 1947, including Turner Valley, had a total output of 19,000 b.d. in 1948, 7% of the country's requirements. As a result of the development of the Leduc–Woodbend and Redwater fields and later discoveries, potential productive capacity of western Canada at max efficient production rates is currently 100,000 b.d., but production is expected to remain at 60,000–70,000 b.d. for some time due to transport problems. Canada's domestic requirements are approx 320,000 b.d.

A pipeline is to be built from Edmonton, Alberta, to Superior, Wisconsin, whence oil will be shipped to the Sarnia refinery in Ontario. The line is scheduled for completion in spring 1951, and its initial outflow at Superior is expected to be 50,000–60,000 b.d.

The economy of Canada's oil development is briefly discussed. C. A. F.

2056. Petroleum developments in Central America and the Caribbean in 1949. R. C. Harris. *Bull. Amer. Ass. Petrol. Geol.*, **34** (7), 1390–2.—Adverse petroleum legislation in Guatemala caused the withdrawal of the three oil companies engaged in oil exploratory work in 1949. The local government is considering carrying out its own surveys, and has already done some work on these lines.

In British Honduras surface geological and airborne-magnetometer operations are scheduled as a result of the issue of an oil-exploration licence to the Bahamas Exploration Co. Ltd. in October 1949.

In Nicaragua very little work was done during 1949 with the exception of an airborne-magnetometer survey of the northeast coast and a small amount of surface exploration.

In Panama one well which reached a total depth of 9715 ft before being stopped in igneous rock was drilled near the town of Puerto Armuelles in the province of Chiriqui.

Production in Cuba was limited to three fields producing from serpentine reservoirs at Motembo, Jarahueca, and Bacuranao. The first two fields produced 19,936 brl and 68,956 brl of light oil respectively, while Bacuranao gave small quantities of heavy asphaltic oil.

A wildcat well which was abandoned at 5045 ft in the Lower Cretaceous was drilled at a water location 15 km north-northeast of the town of Cardenas. E. N. T.

2057. Petroleum developments in South America and Trinidad in 1949. M. W. Haas. *Bull. Amer. Ass. Petrol. Geol.*, **34** (7), 1399–428.—In 1949 the daily average crude oil production for South America and Trinidad increased to 1,574,704 brl as compared with the 1,571,005 b.d. produced in 1948.

The most important factors evident during the year are summarized by the author as follows :—

> (1) Venezuela continued to maintain its position as the second producing nation in the world and the largest exporter of crude.
>
> (2) The absence of strikes in the petroleum industry throughout the year enabled Colombia to establish an all-time production record.
>
> (3) In Peru, the intensification of development in existing fields resulted in a production gain of 5%, the highest daily rate since 1938.
>
> (4) The completion of distribution and refining facilities allowed Bolivia to step up crude production by 46%.
>
> (5) In November 1949, Chile became an oil-producing country when the Cerro Manantiales field was placed in production.

Details of production and exploration work in the various countries of South America are given, and the following are the individual production figures in b.d. for the specific countries during 1949 : Argentina, 65,732 ; Bolivia, 1,861 ; Brazil, 299 ; Chile, 126 ; Colombia, 81,216 ; Ecuador, 7,300 ; Peru, 40,537 ; Trinidad, 56,484 ; Venezuela, 1,321,149. E. N. T.

2058. U.S. firms cut production in Venezuela. H. Ozanne. *World Oil*, Apr. 1950, **130** (5), 234.—American producers are cutting production in Venezuela to obviate the possibility of U.S.A. oil restrictions. British producers are increasing production.

In 1949, Venezuelan production averaged 1,325,491 b.d., 13,000 b.d. less than in 1948. 1950 production is expected to be 150,000 b.d. less than in 1949.

Uncertain demand and lower prices caused a reduction in exploration in 1949. Of the fifty-three wildcats drilled, fifteen found oil, two gas, and thirty-six were dry. The Sibucara well, 6 miles west of Maracaibo, found 37° Cretaceous oil and produced 8000–10,000 b.d. during 1949.

Eight wells have been drilled in the Ruiz field, about 12 miles south of Valle de la Pascua. Total production averages 4500 b.d. of approx 28° oil.

A number of discoveries were made in Anzoategui, Guarico, and elsewhere.

The refinery at Punta Cardon on the Paraguana peninsula increased the country's refining capacity by 55,000 b.d. Refineries are being completed at Amuay on the Paraganan peninsula, and at Puerto la Cruz. C. A. F.

2059. Petroleum developments in Europe in 1949. F. E. von Estorff. *Bull. Amer. Ass. Petrol. Geol.*, **34** (7), 1429–56.—This paper discusses the oil developments in the countries of western Europe, including Denmark, France, Germany, Great Britain, Italy, Netherlands, Portugal, and Spain.

Production in western Europe increased from approximately 8,650,000 brl in 1948 to 11,088,000 brl in 1949, an increase of 28·2%. This increase was due to generally improved working conditions in all of western Europe and to intensified drilling for oil with more modern equipment aided by the Marshall Plan. A high ratio of discoveries in relation to the number of exploration wells drilled was recorded in western Germany, where one new field was discovered for every ten wildcats completed during 1949.

Encouraging results were also reported from the Netherlands, France, and Italy. No accurate data are available for eastern Europe. E. N. T.

2060. German crude output up. Anon. *Petrol. Engr*, June 1950, **22** (6), B-72.—German production is expected to rise from 635,000 tons in 1948 to 1,090,000 tons in 1949–50, despite high production costs. Western Germany now produces about one-third of its domestic requirements.

Centre of production is shifting from the Lower Saxony fields in the Hanover area to the Emsland fields. C. A. F.

2061. The mechanism of hydraulic flow in oil reservoirs. Z. Wilk. *Nafta*, May 1949, **5**, 117–19.—Efficient production is more common in the U.S.A. than in the U.S.S.R. or Poland, but U.S. fields are often running dry. This doesn't mean that there is no oil in the rocks of " dry " wells but that proper methods of displacing the oil must be found. The forces holding oil in the rock are those of surface tension. Gas or water can be used to displace oil. M. S.

2062. Oil progress in Yugoslavia. E. A. Bell. *World Petrol.*, June 1950, **21** (6), 44.—Yugoslavia is believed to have produced 340,000 metric tons of oil in 1949. Most of this oil came from the Donja Lendava area in northeastern Slovenia, 14 miles north of Cakovec on the Hungarian frontier. There was some development of the Goilo area in northern Croatia. Prospecting is going on in the regions of Kakanj, Tuzla, and Kreka, and near Nish.

Questions of supply of equipment, refineries, and relations with other countries are discussed. G. D. H.

2063. Petroleum developments in Middle East and adjacent countries in 1949. R. C. Kerr. *Bull. Amer. Ass. Petrol. Geol.*, **34** (7), 1475–91.—The yearly rate of production from the Persian Gulf–Mesopotamia Valley–Middle East countries had steadily increased during the past few years, but the most spectacular change during that time has been the enormous increase in proven reserves and in the rate of discovery of such reserves.

The excellency of the geological work throughout the entire area is revealed by the very small number of exploratory wells that have been drilled to prove the existence of the enormous reserves known at present and by the very high percentage of discoveries per exploratory well.

Petroleum production in the Middle East and adjacent countries covered in this report was a little more than 514 million brl in 1949, an average of about 1,408,000 b.d. Of this production, 1,400,000 b.d. came from the Persian Gulf–Mesopotamia Valley basin, with some small production from the Punjab area in India, a very small

amount from the Brahmaputra basin in Assam, and nothing from the old Irrawaddi Valley fields.

Some exploratory drilling was carried on in each of the major areas, and as a result, one new field was discovered in Iraq and two in Saudi Arabia. New producing zones were also revealed by deep tests in Iran and Qatar. E. N. T.

2064. Qatar becomes an exporter. Anon. *World Oil*, Apr. 1950, **130** (5), 230.—Nine wells have been completed in the Qatar field, and a 73-mile 12- and 14-in pipeline to the port of Umm Said has been constructed. Each well produces through well-head separators to a central multi-stage separator at Khatiyah, from where it is pumped to Umm Said marine terminal. Five 130,000-brl tanks have been built at Umm Said, and five 148,000-brl tanks are under construction.

Eocene limestone outcrops and shows very low dips. The structure is an anticline which has 300 ft of closure at surface. Production is from the Zekrit lime at approx 5100 ft.

Drilling procedure is briefly discussed. C. A. F.

2065. Petroleum developments in Africa in 1949. H. D. Hedberg. *Bull. Amer. Ass. Petrol. Geol.*, **34** (7), 1457–74.—Although Africa has 20% of the world's total land area, it has to date only produced 0·2% of the world's oil, due to lack of exploratory development and generally unfavourable geology. There are, however, a number of marginal marine embayments and narrow sedimentary coastal fringes which are potential petrolem reservoir areas, as well as the Atlas geosynclincal belt.

During 1949, petroleum production in Africa totalled 16 million brl, which is the highest total so far recorded. More than 99% of this production was from Egypt, the small remainder coming from French Morocco and Algeria. Exploration during the year was carried out in Algeria, Egypt, Ethiopia, French Equatorial Africa, French Morocco, and Tunisia. Geophysical and geological exploration for petroleum was in progress in Algeria, Cameroons, Egypt, Ethiopia, French Equatorial Africa, French Morocco, Madagascar, Mozambique, Nigeria, Tunisia, and Uganda. This work in party months was approx as follows : seismograph, 46 ; gravity, 68 ; ground magnetometer, 17 ; airborne magnetometer, 3 ; telluric prospecting, 32 ; surface geology, 124 ; core drilling, 12. Extensive new oil-concession applications were made in Tunisia. E. N. T.

2066. Oil production in Indonesia. J. Grindrod. *Petroleum*, Mar. 1950, **13** (3), 57–60.—In consequence of war and post-war damage crude oil production in the Far East is still very much less than pre-war production. Consumption is now 35% higher than in 1939, and is steadily increasing. Much depends therefore on the development of the oil industry in Indonesia, the greatest source of oil in the area.

The paper gives a brief outline of the oilfields and refineries, the effects of Japanese occupation and subsequent recapture, and of exploration in Indonesia, especially in New Guinea. R. E. P.

2067. Petroleum developments in Far East in 1949. G. F. Barnwell. *Bull. Amer. Ass. Petrol. Geol.*, **34** (7), 1492–501.—The total oil output of the countries of the Far East amounted to approx 195,000 b.d. in 1949.

In China it has been reported that most of the personnel of the Chinese National Resources Commission, who are responsible for development of the petroleum resources of China, have been taken over by the Ministry of Fuel Industry of the Central Government of China, and since the Laochunmiao field is the only major source of crude production in China, it is assumed that operations in this field continued throughout 1949, with production at the rate of 2000 b.d.

Some geophysical work has been done in the flat coastal regions of western Formosa, and it is thought that about 15,000 b.d. of oil were produced from the small local fields.

With the continued aid and advice of the Petroleum Resources Development Promotion Council, which was formed during the last half of 1949 to replace the Petroleum Exploration Advisory Group of the National Resources Section of the Occupation Forces, the oil production of Japan has shown a small but steady increase throughout 1949. The total production of Japan reached 4500 b.d. during October 1949, and

averaged 3750 b.d. for the year, as compared with a daily average of about 3050 brl during 1948.

In the Philippines, the Philippine Development Co. drilled two wells on its lease in the Bondoc Peninsula, province of Quezone, prior to 1949, and a third well during this year. As in the case of wells Nos. 1 and 2, caving and heaving shale seriously interfered with drilling progress, but the well reached the final depth of 5536 ft. Twelve zones were tested between 1845 and 4300 ft, but no commercial oil was encountered.

In Indonesia considerable rehabilitation work was possible, and the total production of crude oil in 1949 was 42,221,285 brl, as compared with 31,686,209 brl in 1948.

No wells were drilled in north Sumatra, but six were completed in south Sumatra, and exploration and exploitation drilling in south Sumatra was fairly active.

In Java one exploration well was drilled which was a failure, and in northeast Borneo the completion of the deep test at Poeloe Boenjoe as a producer was the outstanding development during 1949.

In British Borneo, drilling activities in 1949 were considerably lower in the Seria field of the Brunei district than during 1948. Only fourteen wells were completed in this area during 1949 as compared with twenty-two in 1948. One exploration well in the Muri area resulted in a dry hole.

In New Guinea the Klamono field in the Vogelkop area of northwestern New Guinea has accounted for the increase in production from 136,493 brl in 1948, to 1,743,588 brl in 1949. An 8-in pipeline was completed over the 30 miles between Klamono and the sea coast at Sorong in December 1948 and has been in service throughout 1949.

In Papua no commercial production has been developed to date. Exploration drilling and geological and geophysical field work have continued in Papua and the Mandated Territory throughout 1949. The drilling programme of the Australasian Petroleum Co. Ltd. has been accelerated by the use of three drilling units.

In Australia the greatest amount of activity took place in the eastern part of the Great Artesian Basin of central and eastern Australia. Near Roma, where encouraging showings of gas and oil had been found in wells drilled before the war, the Commonwealth Bureau of Mineral Resources and technicians of the Queensland State Government have combined exploration forces with the geologists of four companies holding prospecting permits and petroleum leases in this area to examine thoroughly 1000 sq. miles of the eastern section of the Cretaceous basin. One geological party, one gravity, and one magnetic party have been active in this area throughout 1949. It is reported that a seismograph party will be used in the Roma area during 1950. E. N. T.

2068. Oil producing industry in Japan. L. W. Stach. *Petrol. Engr*, June 1950, **22** (6), B-35.—Oil production in Japan during 1949 averaged 3748 b.d., 22% more than in 1948. During the year sixty-three wells were drilled, of which thirty-four were producers.

Most of the new production was from extensions and exploitation of deep reservoirs in Yabase field, Akita Prefecture, and exploitation of the Karahashi field, Yamagata Prefecture, discovered in 1947.

The most significant discovery was the deep zone VIII at about 4200 ft in the Yabase field, which was proved to extend south at least 12,500 ft from the north end of the field, where it was first found to be productive.

Previous years' exploration activity was maintained during 1949. Palæontological research has made considerable advances.

The efficiency of drilling and production operations has been increased. Preparations are being made for dual completion of wells in the new deep zones in the Yabase field, and experiments are being made to determine the feasibility of secondary recovery by water flooding in the shallow zone III at Yabase.

Production in 1950 is expected to be 50% greater than in 1949. New deep pools in the Karumai field, Hokkaido, are to be explored, and six wildcats are to be drilled in Honshu. The margin of the basin in Niigate Prefecture will be explored for extensions, and new pools in possible stratigraphical traps. Other areas will be explored.

C. A. F.

2069. The search for oil in Papua. J. Pain. *Bulletin (Sydney)*, 28.6.50, pp. 20–1.—Indications of oil in the Papuan area were first reported in 1891, when seeps were dis-

covered near the coast of the Gulf of Papua. The first indication of saturated sandstones was in coal measures in the Buti and Iwaka rivers of Dutch New Guinea. In 1910, coal and oil were discovered in Aitape district.

In Papua proper, oil was first reported from the Kiri area, where oil was noted in gas vents near Opa and Akauba. Subsequent government investigations confirmed these indications and discovered mud volcanoes and seeps covering 900 sq. miles. The first well was drilled in 1913 near Upoia and had a small show at 288 ft. Eight wells were drilled in this area and the " field " produced over 4000 gal.

Systematic search began in 1919, and five wells were drilled on a structure at Popo near the Vailala River, one of which found gas. Heaving shale caused drilling problems. Exploration was suspended in the 1929–30 depression, and was not resumed until 1936, when extensive air surveys and field work were undertaken. In 1939, the first major test was drilled in the Kariava district on the Vailala River. The well was abandoned in 1948 at 12,621 ft after slight shows. A well drilled at Oroi, near Yule Island, found shallow gas, but was abandoned in 1949 at 5516 ft on penetrating steeply dipping beds. Tests are being made at Hohoro, Upoia, and Wana. Tests are planned at Malalaua, Orloli, and Omati.

The Papuan area warrants close investigation followed by drilling on selected structures. Good reservoir rocks have not been found, but there are organic clays in the Miocene and Pliocene, and there is evidence of favourable trap conditions.

C. A. F.

Transport and Storage.

2070. Operation of tanker ships. J. H. Jackson. *I.P. Review*, 1950, **4**, 205.—Tankers play an important part in the work of the main oil companies. At the moment, tanker capacity is about 70% above pre-war (mainly due to an increase in the number of American vessels), but a fair number of the existing tankers are more than twenty-five years old. About 25% of the total tankers used are not owned by oil companies, but are " charter vessels " which are hired for short- or long-service periods. Details are given of the development of tankers, their construction, the way in which demands are estimated and the necessary charger tonnage arranged, tanker regulations and management, and types of cargo. R. H.

2071. 9,000 miles of lines now building in all parts of the world. W. P. Sterne. *Oil Gas J.*, 27.7.50, **49** (12), 202.—Tables show principal U.S.A. and foreign crude oil products and natural-gas pipelines projected, under way, and completed this year.

Of the 9000 miles of line, over 6000 are in the U.S A.

A total of 40,000 miles is planned for the future. G. A. C.

2072. Agha Jari–Mashur line—Part I. Anon. *Fluid Handling*, May 1950 (6), 151–4.—To handle crude from the Agha Jari field, a simple stabilizing unit was erected, consisting of three stages of gas separation at 800, 100, and 15 p.s.i.a. The stabilized crude flowed by gravity to the port of Mashur through a 20–22-in pipe. The thicker-walled 20-in pipe was used in the 5 miles between the flow tank at 1320 ft to the end of the foothills (about 100 ft above sea-level). It was tested to three times the max possible head on account of the possibility of falling rock, and the large temp fluctuations. The jigging, dressing, and welding of lengths is described, and the testing is detailed. D. H.

2073. Agha Jari–Mashur line—Part II. Anon. *Fluid Handling*, June 1950 (7), 195–7.—Corrosion was prevented by meticulous de-rusting by hand chipping, and up to three passes of the cleaning machine, followed by priming and enamelling. After wrapping with bitumenized felt and glass fibre the pipe was lowered into the trench across the 40-mile plain to the coast. Final cathodic protection was given by D.C. welding sets consuming 3·26 kW, but will be replaced by 750 magnesium anodes.

D. H.

2074. Aramco Trans-Arabian pipeline, Part I. Anon. *Fluid Handling*, Feb. 1950 (3), 38–42.—When the 1067-mile pipeline from Abquaiq to Sidon is completed, the

500,000 b.d. it will carry is expected to save 700,000 miles of tanker travel per month. The construction and organization of this pipe is discussed in detail.

One-half of the line is 31 in outside dia with a uniform wall thickness of ¼ in, so that the other half, which is 30 in outside dia, can be fitted inside it to economize in shipping space. The pipe is produced in 31 ft 4 in lengths from steel sheet welded along a longitudinal seam. The yield point is then increased to 52,000 p.s.i. by auto-frettage : a hydrostatic pressure of 2500 p.s.i. is applied, causing plastic deformation increasing the diameter by about ¼ in. The pipe is to work under 32,800 p.s.i. stress.

A short section from Abquaiq to Qatif was built first to test methods overcoming the problems associated with thin-walled pipelines and the peculiarities of the desert terrain. Since it might be covered by dunes at any time, expansion joints were eliminated by anchoring to concrete supports or steel bents.

The unloading of the pipes across the 2½ miles of shallow water was effected by a modification of the " skyhook " : a mechanism used for transporting logs. It consists of two overhead cables on which run a number of petrol-driven hoists, each capable of lifting 10 tons.

The welding of sections by the automatic shield-arc process with the aid of a special supporting clamp is described. D. H.

2075. Aramco trans-Arabian pipeline, Part II. Anon. *Fluid Handling*, Mar. 1950, (4), 91–3.—A description of the difficulties encountered in cutting the trench for the below-ground section of the pipe. Rapid changes from sand to rock demanded almost constant use of ditching machine, rooter, backhoe, ripper, and blasting equipment. Corrosion was checked by alternate coatings and wrappings of asphalt and glass floss, supplemented by cathodic protection. Two 17-lb magnesium anodes in a dry river-bed were found sufficient for up to 7 miles of pipe.

The main pumping station contained two double volute pumps driven at 3600 r.p.m. by a 6000 h.p. turbine. Each was capable of handling the entire capacity of the line, 315,000 b.d. at 800 p.s.i. The capacity of the line, its five intermediate pumping stations, and balance tanks is a total of 7,000,000 brl. D. H.

2076. An international gas pipeline, Part I. H. D. Greenwood and A. P. Scarth. *Fluid Handling*, Jan. 1950 (2), 3–6.—This describes the planning and construction of a 600-mm-dia pipeline to deliver town's fuel gas under 48 p.s.i. pressure from the Alsdorf section of the German gas grid to the Dutch state mines at Limburg. The effect of war damage on industrial plant and other buildings gives an idea of the initial difficulties of construction. Since the region was liable to subsidence, the trenching and bedding of the pipe are special. Details of the method of forcing pipe sections through railway embankments without interrupting traffic are given. D. H.

2077. An international gas pipeline, Part II. H. D. Greenwood and A. P. Scarth. *Fluid Handling*, Feb. 1950 (3), 49–54.—Article continues with practical details of welding up the bell-and-spigot joints which allow for subsidence and temp changes. Testing on completion consisted of physical examination under working pressure, and a leakage test in accordance with the standard method of the German Institution of Gas Engineers.

Volume metering was by orifice meter and ring balance recorder, and continuous records of the calorific value and density are made. D. H.

2078. New method developed to identify interfaces in product pipe line. A. P. Howell and R. K. Bond. *Oil Gas J.*, 13.7.50, 49 (10), 66.—The method for following the interfaces (boundaries) between products moving through a pipeline, employed by the Salt Lake Pipe Line Co., uses very minute quantities of a radioactive isotope tracer injected into the line each time a product is changed.

Conventional laboratory instruments re-designed for industrial use were installed at stations along the 566-mile line to measure the radiation at the interface.

No appreciable amount of radioactivity remains in the products whose interfaces have been traced with the isotope, mainly because of great dilution and also because of its self-destroying nature.

Usual precautions of shielding, etc., are taken with injection equipment.

G. A. C.

2079. Mastic-type pipe coatings. G. N. Scott. *Oil Gas J.*, 27.7.50, **49** (12), 283.—The use is outlined and results described of certain highly informative tests which can be made upon single coatings in service.

Methods include examination of the coated line by the Pearson discontinuity locator, and measurement of average conductance of the coating over a fixed length of pipeline.

A table gives data on coating-discontinuity surveys, and the general conclusion is reached that the largest proportions of " holidays " found in coatings could have been avoided by inspection and are thus classified as construction errors. G. A. C.

2080. Bending moments and leakage at flanged joints. Part II. R. G. Blick. *Refiner*, 1950, **29** (5), 119–22.—Assuming that a bending moment on a flanged joint will be restrained exclusively by a re-distribution of the gasket loads; and that each circle defined by the gasket surface remains plane at the flange faces; and either the unit load distribution has the customary " triangular " pattern or some other pattern; two mathematical relationships are derived to obtain the maximum possible bending moments conceivable without leakage. By plotting these bending moments against internal hydraulic pressure, " leakage " envelopes are obtained. R. W. G.

2081. Bending moments and leakage at flanged joints. Part III. R. G. Blick. *Refiner*, 1950, **29** (6), 129–33.—A gasket subjected to a decreasing pressure is " stiffer " than one subject to an increasing load. This results in a shift of the " neutral " axis towards the " tension " side of the centroid.

Relationships are developed for correcting the leakage envelopes for change in bolt load. If formulæ previously given place moment-pressure condition well within the leakage envelope then correction is not necessary. R. W. G.

2082. Expansion joints—their maximum spacing. R. G. Blick. *Refiner*, 1950, **29** (7), 135–6.—Simple mathematical expressions are formulated to indicate max spacing of expansion joints as limited by the support of the weight of pipe and contents. The exact form of the equation depends on the type of support employed. R. W. G.

2083. Are pressure vessels too thick? B. Miller. *Chem. Engng*, 1950, **57** (1), 95–8.—Standards laid down during the last century are criticized in the light of present knowledge of metals. In the same way as the code for pressure piping was revised in 1935 and 1942, it is urged that pressure-vessel design rules are revised. An example is given of gas cyls at present safely working under 2240 p.s.i. Calculating by the conventional equation

$$P_{max} = \frac{S_{max}\,(2R_0t - t^2)}{2R_0t^2 - (2R_0t - t^2)}$$

where P_{max} = max allowable working pressure,
S = tensile stress = 25,000 p.s.i.,
R_0 = external radius of cylinder = 12 in,
t = min wall thickness = 0·448 in,

the max pressure allowed is 950 p.s.i.

The pressure piping code equation gives a more reasonable figure :—

$$P_{mt} = \frac{0{\cdot}9\,Kt_n}{R_0}$$

where P_{mt} = max test pressure,
K = stipulated min effective yield strength,
t_n = nominal wall thickness = 112½% min,

max test pressure = 3072 p.s.i.,
actual test pressure was 2800 p.s.i., and working pressure was 2240 p.s.i.

It is also recommended that thick-walled pressure vessels are designed so that the max safe pressure is that required to make the outer surface plastic, not the inner surface. To do this it is necessary to know the complete stress–strain behaviour of the metal to allow for strain-hardening. D. H.

2084. Line pulse dampener uses cooling coil and seal liquid. Anon. *Petrol. Process.*, 1950, **5** (5), 519.—A Pulsation Dampener for use on fluid streams at high temp covered

by U.S.P. 2,501,804, 28.3.50, assigned by C. F. Yates and C. B. Nolte to The Fluor Corp., Los Angeles, California, is briefly described. The dampening diaphragm is protected by use of a water-cooler, and if necessary a seal liquid separating the line liquid and diaphragm. D. W. F.

2085. New processes for filling and emptying tank cars. R. O. Worth. *Erdöl u. Kohle*, 1950, **3**, 275–8.—Description with drawings of a portable rig for filling and emptying rail tankers. Oil is transferred by gear pump (30 m^3/hr) and is passed through flow-meter which can be pre-set to shut off flow at specified quantity, thus eliminating weighing of cars. Top filling is usual, but bottom outlet can also be utilized, or both simultaneously. Emptying can alternatively be carried out by gravity, through improved metallic conduits, with a sight glass fitted to the pipe-riser. For viscous products requiring to be heated, a new type of immersion heater is described in which oil is heated by hot-air coil, exhaust air therefrom being used to agitate the oil. Air is compressed by a 20-h.p. compressor and blown over a 15-kW element before entering heater, which is then lowered into car. For emptying entire trains a larger non-portable installation of a similar type can be used. V. B.

2086. Warming of rail–road cisterns. S. Rachfal. *Nafta*, Apr. 1949, **5**, 90–3; May 1949, **5**, 120–4; June 1949, **5**, 145–50.—Over 65% of crude and all products in Poland are moved by rail. In winter many heavy products solidify, and quick warming of railcars saves time and money. A railcar can be emptied in time $t = \frac{8Lr^2}{3\mu f\sqrt{gr}}$ sec, where L and r are the dimensions of the railcar, f = area of outlet, μ, coefficient.

μ depends on kinematic visc v for warming the railcars steam line or in coil, circulating, electric or pressure heating can be used. Of these live steam seems to be most popular. Portable heaters are used as described. Two diagrams are included and formulæ enabling the calculation of: (1) final required temp, (2) specific heat of products and (3) quantity of steam required. A table gives % wax content in relation to pour point.

Heat losses are calculated according to formulæ given. Some relevant points are that pressure of steam should not exceed 45 lb, steam should be dry, three pipes are necessary because their dia is critical to adequate circulation. Care must be taken to avoid frothing.

For heating with steam in a coil portable coils are sketched, designed by Tchekmarev, Glastowiecki and by Meédveév. Steam heating in coils does not raise the level of oil in the railcar. Time required is about 5–6 hr for a railcar of capacity 25 cu. m. of oil of pour point 60° F, visc 1·5° Engler at 80° F approx, at − 10° C external temp. Steam used at 60 p.s.i. This result is obtained with the help of several formulæ which are given. Permanent fixtures have an area of over 30 sq. m. for large, and of 5–8 sq. m. for small railcars. Knowing the distance the railcar has to travel it is possible to load it up at a temp high enough to enable the load to be pumped out without delay. Good insulation of such railcars is necessary.

Circulating method, otherwise known as "hot washing," is briefly a combination of internal and external heating. A portable heater melts the top layer of product, which is then taken through a heat exchanger, its temp raised considerably and pumped at fairly high pressure into the load through the bottom of the railcar. A safe temp for the re-entering product must be some 15° or 20° C below flash point. The disadvantage of this method is the capital expenditure involved.

Electric heaters of two designs are described, and power consumption for certain sets of circumstances is worked out. Some points worth while noting for convenience and safety are given.

Use of high pressure shortens the time required for heating by approx 60%. In the U.S.S.R. the use of pressures up to 2 atm is permitted.

General notes on planning of a ramp are appended. They also show the advantages and disadvantages of all methods. A list of Soviet books on the matter is given.

M. S.

2087. "Thermos jug" tanks for lube stocks now in service. Anon. *Refiner*, 1950, **29** (5), 88.—For transportation of lube oil stocks between Houston and New Orleans a new river-barge has been built having four glass-fibre insulated tanks. By this means the lube oil loaded at 110–140° F reaches its destination, six days later, at a temp of

90° F or more. As an added precaution the tanks are equipped with steam-coils which can be supplied by shore steam. Piping and pumping arrangements allow for simultaneous discharge of two different cargoes. R. W. G.

2088. Pumping solids in a chemical works. S. Smith. *Fluid Handling*, Apr. 1950 (5), 112–13.—An economic balance shows that fluidization provides a very much cheaper method of handling finely divided solids for intra works transport than by bagging. Precautions to prevent the clogging of the lines are detailed. D. H.

2089. Packaging for the oil industry. D. A. S. Williams. *Chem. Prod.*, July 1950, **13** (8), 318.—The importance of correct packaging procedure is often overlooked by reason of the greater emphasis placed on endeavours to improve the quality of products and on making the article more attractive to the user from a cost point of view. This is a mistaken attitude, and often results in the products being received by the customer in a quite unusable condition.

There is a definite need for education in the science of correct packaging procedure, and oil companies can do much to help themselves and others by asking their suppliers of equipment, etc., to quote a price for the goods delivered f.o.b. with a separate price and specification for the packaging.

The question as to what is a reasonable cost for packaging is not easy to answer, but the economic level can be assessed from statistics showing losses due directly to inferior packaging. This consideration also applies to production losses caused by deterioration of petroleum products in storage.

The many variables which influence the choice of a package specification fall into the following groups :—

(*a*) Those produced by conditions not directly controllable by the user of the goods, *e.g.*, transport, handling, and storage conditions.

(*b*) Those which are governed by the requirements of the user. O. M.

2090. Underground storage and migration of natural gas. F. E. Vandaveer and J. J. Schmidt. *Oil Gas J.*, 27.7.50, **49** (12), 270.—The use of underground storage of natural gas in wells to allow for meeting peak loads, pipeline failures, and to permit a good transmission pipeline load factor is reviewed.

Five possible structures for underground storage include depleted or partially depleted dry gas and dry oil fields, excavations in rock layers, cavities in salt layers, and steel pipe or bottles to hold gas under 2000 p.s.i. buried underground.

The economics of underground storage shows that the method is much less expensive than any other. Tests are made to determine whether or not migration of gas to other producing wells is taking place. G. A. C.

2091. Storage of L.P.G. fuels at low pressure. C. V. Spangler. *Refiner*, 1950, **29** (6), 86–8.—A granular absorbent has been developed which should result in safer storage and transport of liquefied methane, propane, or butane. 1 cu. ft. of the absorbent can absorb 500 standard cu. ft. of methane, and while it appears wet no flow is observed when the absorbent is spilled out on to the ground. In the case of river- or sea-transport propane, for example, could be loaded at its boiling temperature −44° F. During the voyage the small amount of vapour given off due to heat leaks could be vented and used as a fuel. In the case of rail transport, the fuel would need to be transported in a pressure vessel as at present, but the absorbent would mean greater safety in the case of an accident. Photographs show the sudden flash which occurs when two quarts of methane are ignited, and the slow gentle burning of the same quantity of absorbed methane. R. W. G.

Refinery Operations.

Refineries and Auxiliary Refinery Plant.

2092. Heysham Refinery—A study in adaptability. A. W. W. Kirby. *J. Inst. Petrol.*, 1950, **36**, 255.—In February 1948 the plants of the wartime Trimpell factory at Heysham, which had been used for the production of 100-octane aviation spirit by the

high-pressure catalytic hydrogenation of a gas oil feedstock, were purchased by the "Shell" Refining and Marketing Co. Ltd. and re-designed for the conventional distillation of crude petroleum at an annual throughput of 1½ million tons. This involved the reorganization of the storage and distributional facilities to handle a daily quantity of oil three times as great as that for which these facilities had been designed. The original functions of the various plants are recounted briefly, and the plants as they are now operating are described in detail. A. R. W. B.

2093. Mayoville plant serves "golden trend." A. L. Foster. *Petrol. Engr*, Feb. 1950, **22** (2), C-7.—Five producing companies handling six pools have collaborated to run the Garvin County plants. Of the three plants, two are compression and absorption plants, and the third, together with the usual natural-gasoline-extraction units, has compression and absorption plants. Absorption oil is circulated from the main plant to the two subsidiaries 7½ miles away, and the rich oil is all processed at the central plant. Due to the scarcity of water, four vertical heaters supply the heat directly to the rich oil and provide heating oil for reboilers, etc. In the stripping column, the light hydrocarbon vapour overheads are preheated and fed into the still a few trays below the rich oil inlet while for final stripping de-ethanized overhead heated to 500° F is fed in below the top tray. G. K. A.

2094. Wax and lube oils shine at Cit-Con. J. A. Lee. *Chem. Engng*, 1950, **57** (3), 94–6.—Many interesting features of the Lake Charles, La., refinery of Cit-Con Oil Corp. are noted in this article. The feed is topped Texan crude from a nearby refinery owned by the same company. Products are 6000 b.d. lubricating oil and 70 million lb of wax per annum. By-products are returned to the other refinery.

The crude is fractionated under vacuum in a column fitted with "shower" trays to reduce the pressure drop. Improvements on the normal furfural and Duo-Sol refining schemes are described. Wax is removed from the raffinates with a solvent composed of methyl ethyl ketone, benzene, and toluene.

The lubricating oils are finished by a clay treatment, and waxes are acid treated, neutralized with caustic soda, and allowed to percolate through bauxite. Product storage tanks are conditioned to reduce oxidation and condensation from the humid atmosphere.

An induced-draught multistage cooling-tower cools 51,000 g.p.m. of water from 117° to 92° F at a wet-bulb temp of 87° F. D. H.

2095. Proportiometer pumps at new petroleum chemicals plant. G. J. E. Howard. *Fluid Handling*, Dec. 1949 (1), 29–31.—With the general trend of industries handling liquids to change from batch to continuous chemical treatment, the need is increasing for a dependable pump to supply two liquids at a fixed ratio, independent of the volume. The several makes of proportiometer pumps can be classified into variable-stroke types and those with constant stroke employing the differential piston system. The latter are used in the new plant at Partington, belonging to Petrochemicals Ltd. The principle described is that two pistons operate in a common cyl-block of the appropriate capacity and material, having one suction and one discharge. They are driven at a constant speed, but the phase between them is continuously variable by means of a differential gear whose central bevel is moved 90°. When both act together the pump delivers its max rating, and when moving in opposite directions will pump no liquid.

There is a description of applications to gas-washing plant, the boiler-house, and in the manufacture of *iso*propyl alcohol, ethanolamine, and ethylene glycol. D. H.

2096. Refinery shop—layout and operation. R. Haldane. *Refiner*, 1950, **29** (5), 79–87. (*Mid-Year meeting of A.P.I. Div Refining, Cleveland, Ohio.*)—To attend to all plant maintenance work, Shell Oil Company's Houston Refinery has built a new 98,000 sq. ft. maintenance shop. Chief objects of the design and organization are speed in passing a job through the various sections of the shop. A description of the shop and method of identification of the job are given, together with a list of all machine tools, including two gasholt dynamic balances, a cylindrical grinder, and a horizontal boring mill. A cleaning building is provided to reduce to a min the amount of dirt and oil brought into the building. Skilled craftsmen are obtained by a plant training

scheme. It is difficult to evaluate the returns of such an installation except by showing that manpower and downtime have been reduced. R. W. G.

2096a. Shell's new refinery maintenance shop integrates all crafts under one roof. R. Haldane. *Petrol. Process.*, 1950, **5** (5), 483–89.—(See Abstract No. 2096.)

2097. British refineries (No. 7). Heysham refinery of the Shell Refining and Marketing Co. Anon. *Petroleum*, June 1950, **13** (6), 143–6.—During the war the refinery was used for production of 100-octane spirit from gas oil feedstock by high-pressure catalytic hydrogenation. In 1948 it was reorganized to process asphaltic Kuwait crude, producing motor gasoline, gas oil, and fuel oil. Details, with diagrams and photographs, are given of the conversion. R. E. P.

2098. The refinery of the Royal Dutch Shell group at Rotterdam (Pernis). A. H. S. Welling. *Ingenieur*, 21.7.50, **62** (29), A359.—A description of the Shell Refinery at Pernis from the layman's point of view. R. R.

2099. Gulf Oil's flare stacks are designed to solve three important problems. Anon. *Petrol. Process.*, 1950, **5** (5), 511, 514.—The waste-gas-stack design developed and used by Gulf Oil Corp. is described with diagrams. The 20-in-dia stack has a 52-in-dia burner lined with 4½-in refractory. Three stainless-steel pilot jets in this head are ignited by a torch raised from ground level by a stainless-steel cable. Claimed for this design are safe and efficient pilot burners, protection of operating personnel, and long flare-tip service life. D. W. F.

2100. Refinery flare stack ignition devices. O. L. Clevenger and W. A. McElhannon. *Refiner*, 1950, **29** (3), 148–9.—A small amount of natural gas is introduced into a ¾-in tube near the top of the flare stack. This gas is led into a 10-ft-long section of 2-in-dia pipe, where after mixing with air the gas is ignited by a 6½-V, 60-amp heating element. The flame travels to the top of the 2-in-dia pipe and ignites the pilot light. A suitably placed thermocouple indicates whether pilot is burning. Advantages claimed: no explosion hazard even if air is present in ignition line; low-voltage circuit avoids insulation difficulties. This unit was developed by the Baytown Refinery of Humble Oil and Refining Co., and has been in continuous use for eighteen months on stacks ranging 200–300 ft in height. R. W. G.

2101. Refinery develops improved procedure for removing coke from soaker drum. Anon. *Petrol. Process.*, 1950, **5** (5), 514–15.—A new procedure for removing coke from soaker drums developed by a large Illinois plant is described. A hole is drilled through the coke from top to bottom, using an air-motor and a special 5½-in-dia carbide-tipped drill supported by 4-ft lengths of 1-in pipe with steel couplings. The hole is then enlarged using a chain knocker or 8½-in- and 12-in-dia drills. Remaining coke is removed by workmen supported on a swinging collapsible scaffold, the coke being pushed out of the bottom of the drum through the drilled hole. D. W. F.

2102. Modern processes in the oil industry. C. Walther. *Erdöl u. Kohle*, 1950, **3**, 327–30.—Contemporary trend in pet processing is towards the use of continuous plants in which the material being treated (*e.g.*, oil, gas) is processed in one vessel whilst the treating medium (*e.g.*, cat, chemical reagent, solvent) is passed to a separate vessel where continuous regeneration takes place. Following (American) processes are described in outline, with sketches; gas purification, gasoline desulphurization, hypersorption, hydrocol, cat cracking (moving bed and fluid flow), thermofor pyrolytic cracking, continuous coking, continuous oil-shale retorting. V. B.

2103. Stud welding simplifies refractory work. Anon. *Refiner*, 1950, **29** (4), 151.—Special ½ × 4-in steel studs with 2-in-square bases welded to the inner shell are used to support special tongue-and-grove refractory tiles in a catalyst regenerator of the Sun Oil Co's new Toledo refinery. R. W. G.

2104. Operation of oil–water separator at Trenton plant. C. F. Miller. *Refiner*, 1950, **29** (5), 135–7. (*15th Mid-Year Meeting of A.P.I. Div. Refining, Cleveland,*

Ohio.)—Since 1929 the Socony-Vacuum Oil Co. Inc., Trenton, and the Michigan Stream Control Commission have worked together to avoid pollution of the Detroit River by the refinery sewerage. An A.P.I. separator with 2500 g.p.m. capacity was installed. The general flow pattern is as follows. Refinery sewerage, together with any return water from the storm pit, enters a preliminary sump, where sludge is removed and some oil is separated. Water from here is pumped to a coalescer. During storms any excess flow is diverted to a storm pit, from which it is returned when conditions allow. From the coalescer, the water enters the A.P.I. separator. Oil is skimmed from the water and taken through a heat exchanger to a settling tank and then to a storage tank. The effluent water from the separator is removed to the Detroit River. R. W. G.

2105. Power plants for modern refineries. Part I. T. G. Hicks. *Refiner*, 1949, **28** (12), 113–16.—Up to twenty years ago refinery power-plant design was influenced by the availability of low-cost fuels and low demand for electricity. Steam pressures were relatively low, 200 p.s.i., and during periods of low production steam was exhausted to the atmosphere. Central stations and other industrial plants were well ahead in this respect. In the modern-type plant, however, steam is generated at 1350 p.s.i., passes through two superposed 10,000-kW turbines then to a 400-p.s.i. header. This is used for refining processing or reduced, through further turbines or auxiliaries, to a 100 p.s.i. header. With this development, steam-driven auxiliaries have been replaced by motor-driven units. Figures are given which illustrate this development in refinery power-plant. R. W. G.

2106. Power plants for modern refineries. Part II. T. G. Hicks. *Refiner*, 1950, **29** (2), 129–32.—Some refineries, with high process steam demand and low electricity demand have successfully co-operated with central utilities. The utilities generate high-pressure steam, which is reduced through turbines and passed to the refineries. The refineries, in return, provide waste fuel such as acid tar, pitch, refinery gas, and coke. A power-plant for a petrochemical plant is described.

Although refineries in the twenties and thirties lagged in matters of thermodynamic balance, they led the way in outdoor and semi-outdoor plant design. Even with winter temp of −30° F outdoor plants have operated successfully. At least $5/kW has been saved in construction costs, and many operating men prefer the cleaner and better ventilated outdoor plant. The important factors in outdoor power-plant construction are discussed. R. W. G.

2107. Power plants for modern refineries. Part III. T. G. Hicks. *Refiner*, 1950, **29** (5), 143–5.—To-day, waste heat is hunted down and made to do work. Catalytic units generate 20,000–60,000 lb/hr of 450-p.s.i. by-product steam. Instead of using power-plant steam it is often more economical to produce process heating steam by means of waste heat. Convenient headers can be used to provide steam during periods when waste heat is not available. Natural-gas expansion turbines are finding more use in refineries where their low first cost, high efficiencies, and lack of fire hazard make them ideal.

End of series. R. W. G.

2108. Depressuring systems in refineries. N. E. Sylvander and D. L. Katz. *Refiner*, 1950, **29** (3), 140–5.—It has been shown that a metal plate exposed to fire can reach a temperature of 1300° F in 4 min. At this temp and subject to a pressure of 15,000 p.s.i., the rupture time is 2 min. If then a pressure vessel should be subjected to fire it is probable that the conventional pressure-relieving systems, *i.e.*, pressure-relief valves or rupture discs, would not be adequate. A pressure-relief valve will limit only rise in pressure, and a rupture disc will not operate until an excess pressure has built up. Other accidents, *e.g.*, vessel plate or seam failure, may also require a quick pressure release. Various electric, hydraulic, or manual quick-operating valves are described. R. W. G.

2109. Maintenance practices in a small refinery. J. S. Pfarr and others. *Refiner*, 1950, **29** (5), 105–10.—A small refinery carries much the same processing equipment as a large refinery except in regard to the amount of spare parts carried and the

staffing of the maintenance department. To keep pace with technological improvements the small refiner must buy his equipment at the minimum cost and buy essential spares and duplicate equipment later. As compared to the larger refinery, the smaller refiner usually has higher capital costs and higher running costs per unit of product. To compete, the small refiner must have flexibility in his organization. The authors describe the organization in their own small refinery 18,500-b.d. crude unit ; 5000-b.d. T.C.C. catalytic cracking unit, etc. Flexibility is demanded from staff. The painters attend to insulation, and one is also a welder. Neighbouring small refineries loan staff to overcome bottlenecks. Operators take care of day-to-day upkeep of their units. Plant cleanliness is insisted upon, and by this means small leaks, etc., are noted and attended to, and a favourable impression is made on prospective customers. Only a small maintenance staff is retained, and depending on their availability constructional work is contracted or part contracted out. Large plant is inspected and reported on regularly by outside firms or the makers, who make this service available. Shutdowns are planned at least six weeks before, when as many of the staff as possible meet to discuss possible requirements and preparatory work. A further meeting is held five weeks later to discuss job allocation during the overhaul. R. W. G.

2110. Calculation of fractionating absorbers. L. Kniel. *Bull. Ass. franç. Tech. Pétrole*, 1950, (82), 41–56.—Increased use of liquefied pet gases has made absorption fractionation an important refinery process, to ensure adequate separation of C_1–C_2 from C_3–C_4. A fractionation absorber can be considered as a fractionating tower in which reflux, introduced above, is not in phase equilibrium with issuing gases. Sample calculations and flow diagrams are given for typical cases, using 230–350° F absorber oil, and absorber operation is discussed. Unstabilized cracked gasoline can be used as absorber oil for methane removal from refinery gas ; gas and gasoline being thus demethanized together. A supplementary absorber is required in such a case to remove C_2–C_3. A lay-out is also shown for recovery of propane from gas containing 96% CH_4 ; practicability of use of such a gas, however, depends on local economic conditions. V. B.

2111. Short cuts in process design—heat exchangers. P. Buthod. *Refiner*, 1950, **29** (6), 79–83.—Heat-exchanger problems may be classified in three main types : (1) counter-current flow, in which a log mean temp difference applies ; (2) counter-current flow, in which arithmetic mean temp difference is used ; (3) parallel flow. For (1) re-arranging heat-transfer equation gives : $\frac{mc}{UAF} = \frac{\frac{T_1 - T_2}{t_2 - t_1} - 1}{\mathrm{Ln}\left[\frac{T_1 - t_2}{T_2 - t_1}\right]}$ and from an overall heat balance $mc(t_2 - t_1) = MC(T_1 - T_2)$. To simplify handling these formulæ let $X = \frac{mc}{MC} = \frac{T_1 - T_2}{t_2 - t_1}$; $Y = \frac{T_1 - t_2}{T_2 - t_1}$; and $Z = \frac{mc}{UAF} = \frac{X - 1}{Ln\ Y}$; by substitution also obtain $t_2 = t_1 + \frac{(T_1 - t_1)}{D}$. Charts are given for calculating Z or D when X and Y are known. If the operating conditions of an existing heat exchanger are to be altered, then results may be predicted by such formulæ as $X' = X \frac{m'c'MC}{mcM'C'}$ etc. Similar equations are given for type (2). Equations for type (3) are not given, but can be developed. Five examples of change in operating conditions are worked out.

m, M, weights of cold and hot fluids per unit time ; t, T, temperatures of cold and hot fluids ; U, overall heat-transfer coeff ; A, surface area ; F, correction factor for multi-pass exchangers ; $D = (XY - 1)/(Y - 1)$; ′, new conditions. R. W. G.

2112. Tetra cresyl silicate for heat exchange, Part I. Anon. *Fluid Handling*, Dec. 1949 (1), 2–6.—The use of tetra-cresyl silicate (T.C.S.), which boils at 800° F, as a heating medium where high-pressure steam-plant was uneconomical is described in its application to batch spirit distillation.

It is heated to 350–400° F in a three-pass oil-fired tube still made in three standard

units for easy renewal. Heavy fuel oil of 950 sec is heated by steam or electricity to assist the steam atomization. Safety devices cut off the oil supply if the flame should blow back or go out. The T.C.S. circulates at 330 g.p.m. through a 4-in-dia tube to the coils of the three separate stills. Fine control is required to maintain a good-quality product, and this is effected by graduated valves set to a predetermined optimum reading.

The exclusion of moisture from the system is an essential feature of this material, and special precautions are taken to ensure it. D. H.

2113. Tetra cresyl silicate for heat exchange, Part II. Anon. *Fluid Handling*, Jan. 1950 (2), 10–12.—The instrumentation of the heating system described in Abstract No. 2112 is sufficient to enable a heat balance to be made from routine data.

Testing of the system involved a mechanical test of 100 p.s.i. internal pressure, testing for leaks with ammonia and conc HCl. Flanged joints on coils in the stills were tested by filling with water and applying 100 p.s.i. to the coils. Drying of the system with hot air was important because water may form cresol and higher polymers of cresyl silicate. After filling the system and the 750-gal balance tank, a test distillation of water was made before proceeding to food-products manufacture. Routine tests can detect presence of 1 p.p.m. of T.C.S. in the product.

T.C.S. is inert to mild steel and bronze, and because it is used at atm pressure normal packing materials will completely seal the joints. It is not toxic to operators, is non-inflammable, and has good heat-exchange properties. Scaling is negligible, and its very low visc change with temp reduces the starting time. The system seems suitable for close control, and provides an even rate of heating with high temp drops.

D. H.

2114. Analogy between heat transfer and mass transfer—a psychometric study. C. H. Bedingfield, Jr., and T. B. Drew. *Industr. Engng. Chem.*, 1950, **42** (6), 1164–73. (*Absorption and Extraction Symposium, Divn. of Industr. Engng. Chem., Amer. Chem. Soc., Ohio State Univ. Dec.* 1949.)—Psychometric data, obtained with volatile solids as " wet bulbs," are presented to support the analogy between heat transfer and mass transfer. Extensive theoretical treatment is given, and the data are shown to be consistent with those of previous workers, in showing no effect of Reynold's number or temp. A correlation of the mass transfer data is made which shows consistency with heat-transfer data. R. G. T.

2115. Heat transfer in finned tubes. D. E. Mack and A. E. Pitcher. *Heating and Ventilating*, June 1950, **47** (7), 75.—When calculating the heat transfer in finned tubes metal temp is very difficult to evaluate because the tip of the fin is generally at a different temp from the base of the fin. It is suggested that this difficulty can be overcome by using the temp of the base of the fin which can be evaluated and introducing a " fin-efficiency " factor to compensate for using the improper temps. This is explained in detail, and a nomogram is supplied to facilitate calculations. A number of examples are given demonstrating the method of application to different types of fins.

A. S.

2116. Heat transmission in coils. H. Inglesent and J. A. Storrow. *Industr. Chem.*, 1950, **26**, 313–17.—Overall heat-transfer coeff for coils immersed in unstirred liq are shown to be higher than those for single horizontal tubes under the same conditions. Outside surface conductances are probably 70% higher for coils than for straight tubes, but Reynold's numbers up to 15,000 failed to give fully turbulent flow in curved path through particular coil used. A. C.

2117. Application of the membrane analogy to the solution of heat-conduction problems. L. H. Wilson and A. J. Miles. *J. appl. Phys.*, 1950, **21**, 532–5.—A homogeneous membrane, such as a soap film, of any shape supported at its edges obeys the relation $\left(\frac{\delta^2 z}{\delta x^2} + \frac{\delta^2 z}{\delta y^2}\right) = 0$, where x and y are space co-ordinates, and z is the vertical deflection of the membrane. Replacing z by temp, the equation represents steady-state heat conduction in two dimensions. Thus the deflection of the membrane represents the temp distribution throughout the member under consideration, and if the boundary

conditions are known, a model of the heat-conducting member may be constructed. The apparatus which is described for measuring the film is simple and inexpensive.
D. F. J.

2118. Flow of heated gases. A. S. Thompson. *J. appl. Phys.*, 1950, **17** (1), 91–8.—A graphical design method is given correlating the variables involved in the transfer of heat from the wall of a passage to a gas moving at high velocity in the passage. The method uses Reynold's analogy between heat transfer and friction, and covers one-dimensional flow in a passage of variable area and with variable wall temp.
D. F. J.

2119. How solids flow in pneumatic handling systems. A. H. Korn. *Chem. Engng.*, 1950, **57** (3), 108–11.—After discussing qualitatively the forces acting on suspended solids in pipes, basic pressure-drop equations are used to derive a sound basis for correlating the scattered data at present existing. These data are discussed critically, and it is concluded that at present, data are insufficient to make reliable designs.
D. H.

2120. Design of packed absorption and distillation columns. I. H. R. C. Pratt. *Industr. Chem.*, 1950, **26**, 291–5.—Part I covers absorption and stripping columns only. Equation for deducing mass transfer coeff includes factors dependent on liq rate and type of packing. For liq rates below a crit min, viz., when packing has been completely wetted, transfer coeff falls off rapidly. Optimum column dia and packing are affected by both gas- and liq-flow rates. At a given liq flow, increasing gas flow above a certain rate causes rapid increase in pressure drop across packing (loading point), and at still higher rates liq builds on top of packing (flooding point). Generally vapour velocity at flooding is about twice that at loading. Columns are normally designed to operate at about loading point, but other factors, *e.g.*, liq visc, may affect this. Methods of determining packed ht are described, based on (*a*) transfer coeff, (*b*) transfer units. A short account is given of practical problems in design, *e.g.*, methods of supporting packings and distributing liq evenly. A. C.

2121. Critical study of methods for absorber calculation. M. R. Dolez. *Bull. Ass. franç. Tech. Pétrole*, 1950 (82), 57–74.—Following methods of calculating bubble-column absorbers are summarized : " plate by plate," absorption factor (individual), absorption factor (mean) (procedures of Kremser, Horton and Franklin, Edmister), and Sherwood's semi-graphical procedure. All these give similar numerical results, the first four agreeing very closely. Eliminating the more laborious of the methods the three procedures based on mean absorption factor are compared with results obtained in practice, the findings being tabulated. Good agreement is found in all cases for composition of " poor " gas, but considerable discrepancy exists between No. of theoretical plates calculated and actual plates used. The No. of theoretical plates is only of significance for absorption factors in range of 0·5–2. At values $< 0{\cdot}5$ the absorption factor alone is of importance, whilst at values > 2 absorption is almost complete. Calculation of No. of actual plates required can only be very approximate, but absorption factor can be influenced considerably by modifying operating conditions. V. B.

2122. Expansion joints and their application. F. E. Wolosewick. *Refiner*, 1950, **29** (5), 146–150.—In order to minimize the destructive forces from thermal expansion of piping three procedures are adopted : (1) major equipment is allowed to be displaced bodily, (2) expansion is absorbed by flexure of piping or by expansion joints, (3) special cases involving a combination of (1) and (2).

Considerable economies are possible with (1), though it is not practicable where the forces necessary to displace heavy equipment may be too large for other structures to resist. For (2) two types of equipment are available ; sliding sleeves, corrugated bellows, and piping loops for straight expansion ; hinged bellows and use of ells where flexibility is required. Graphs are given for analysis of simple type bends with hinged expansion joints. Construction of various types of bellows-type expansion joint are illustrated. Stress, deflection, and direct forces are difficult to evaluate mathematically with this type of joint. R. W. G.

2123. Seals for rotating shafts. E. F. Boon. *Ingenieur*, 21.7.50, **62** (29), Ch. 43.—It has been generally considered that pump stuffing-boxes should leak slightly to take care of the lubrication and cooling of the packing. However, the development of the mechanical seal shows clearly that a tight seal is possible. Various factors leading to a tight seal with a normal stuffing-box are described, such as a perfectly smooth and true shaft, elastic and impermeable packing material, pressure of packing on shaft being higher than pressure in pump and minimum radial movement of shaft. A precise assembly of packing is necessary to obtain a tight seal. This is possible with special tools, and drawings of these are given in the paper. Special constructions to cope with excessive radial movement of the shaft are also described. R. R.

2124. Thermal design of condensers. W. Glower. *Industr. Engng Chem.*, 1950, **42** (7), 1361–9.—The principles of heat transfer by conduction and convection are applied to development of a rating method for condensers. Treatment is mainly theoretical and although applicable to all types of surface condensers is here applied only to shell and tube condensers. Heat release for the condensing vapour and condensate is shown and the heat release v, temp relation gives parabolic curves showing an increased mean temp difference for vapour and reduced mean temp difference, for condensate. Effect of temp difference, upon heat transfer coefficient of condensation on horizontal tubes is discussed. Effect of condensation on H.T.C. of convection is shown by an approx correction factor applicable to this H.T.C. The case of non-constant heat transfer is discussed, and a combined H.T.C. evolved. Correlation of pressure drop through condenser shell and friction factor is made. R. G. T.

2125. Pressure drop through fixed and fluidized beds—a nomogram. M. Weintraub and M. Leva. *Chem. Engng*, 1950, **57** (1), 110–13.—The important variables affecting pressure drop in fixed and fluid catalytic industrial processes have previously been correlated in the region of viscous flow by the equation

$$\Delta_p = \frac{200G\mu L(1-\varepsilon)^2}{gD_p^2\rho_f\varepsilon^3\phi_s^2}$$

D_p = diameter of sphere of volume equal to particle,
G = superficial mass velocity of fluid,
L = length of packed section of reactor,
ε = ratio of void space to total packed space,
ϕ_s = shape factor,
μ = gas viscosity,
ρ_f = gas density.

This equation is the basis of the nomogram. Its application to transitional and turbulent ranges is made possible by a further nomogram. Previously published data on fractional voids are summarized graphically, and three examples are worked out. Accuracy appears to be between 1 and 10%. D. H.

2126. Thermal insulation in refineries. J. F. Stone. *Petrol. Engr*, Jan. 1950, **22** (1), C-11.—The amount of insulation to use is that thickness, the annual cost of which added to the annual cost of refrigeration, gives the lowest combined total. The average thickness for insulation in modern practice is given in a table for various differences and pipe dia. A table is also given of the properties of modern insulating materials. Condensation on the surface of insulation requires a knowledge of surface resistance. A value of 0·60–0·65 can be taken for almost stationary air, but in winds over 25 m.p.h. the surface resistance is negligible. Knowing the total resistance of the insulation, the surface resistance and the temperature drop, the temp of the surface can be calculated and if this is below the dew point, condensation will take place. Charts are given to calculate the insulation thickness without condensation. Insulation coverings are considered and a table of water-vapour permeabilities of various coverings is included. G. K. A.

2127. Boiler arrangement for economizer washing. Anon. *Mech. World*, 25.8.50, **128** (3319), 175.—With the older type of Yarrow boiler the economizers were placed

above the boiler with the gases flowing upwards through the economizers. The hardest deposit builds up on first few rows of tubes on the gas-entering side of the economizer, and it is very difficult to wash off here as it covers the half of the circumference of the tube facing the oncoming gas stream. In the case of the new boilers the design is better from an economizer washing point of view as the gases flow down through the economizer and the water therefore strikes the same surface as the gases. By means of the improved design it is possible to wash these economizers within two or three days, whereas with the older design the economizer washing takes from four to five days. Tubes in new type of economizers are arranged in banks with inspection doors between the banks, an arrangement which facilitates washing down. Where phosphatic economizer deposits are the chief source of trouble the design of the economizer tubes must be such as to limit the deposit surface temp to below 420° F at all times. A high economizer outlet temp can be attained under these conditions only by using plain tubes at the gas-entering side of the economizer. A. S.

2128. Cylindrical furnaces for the petroleum industry. O. F. Campbell. *Refiner*, 1950, **29** (1), 109–18. (*A.S.M.E. Meeting, San Francisco, June* 1949.)—A detailed discussion of the application of the de Florez, Iso-Flow, and Helical Coil cylindrical furnaces.

Cylindrical furnaces are used for crude topping, vacuum distillation, cracking, high- and low-temp steam superheating, etc. The furnaces utilize radiant-heat tubes for heat transfer, and may be fitted with the normal auxiliaries, *i.e.*, air-preheaters, I.D. and/or F.D. fans. A directional flame control burner is described which is capable of handling refinery gas, natural gas, or heavy fuel oil. Several flow diagrams are presented showing the adaptability and flexibility of the de Florez furnace to both cracking and heating—where different heating characteristics are required. The Iso-Flow furnace is stated to be particularly suitable for small heat duties and for low average temp. The advantages of the cylindrical furnaces are simplicity, flexibility, low space requirement, ease of cleaning, and low capital costs. Efficiencies of de Florez furnaces reported range from 75 to 79·5%.

Some operating data for cylindrical furnaces are given. R. W. G.

2129. High temperature combustion-heated furnaces. M. W. Thring. *J. Inst. Fuel*, 1950, **23** (132), 178.—An analysis of the present position of research into high-temp combustion-heated furnaces indicates interest should be divided equally between application of existing knowledge and discovery of new. Thermal efficiency depends on employing a heating cycle that can make use of the heat in the combustion gases over the range from theoretical combustion temp to room temp and upon the precision with which this cycle is carried out. Existing knowledge which is as yet insufficiently applied includes control of the combustion-gas composition, the use of models to find out how to improve mixing and so shorten flames, and more extensive use of the counter-flow heating system. Benefits which would be derived from better application of existing knowledge can best be assessed by controlled variable statistical trials planned to enable factorial analysis to be carried out. Subjects on which more knowledge is required are the emissivity of luminous flames, general conditions of mixing, and the effect of recycling combustion gases. Many diagrams of furnaces are included. There are twenty-two literature references. D. K.

2130. Carbon as a structural material. A. E. Williams. *Mech. World*, 4.8.50, **128** (3316), 99.—Industrial carbons have been used for many years on a considerable scale, and their applications include turbine gland rings, carbon brushes, and electrodes. In the form of diamond, carbon has long been applied to wire-drawing, grinding, and cutting of metals, etc. Recently carbon has been applied successfully as a structural material in the sphere of chemical engineering. Carbon has excellent resistance to all but strongly oxidizing chemicals, can be heated and cooled rapidly, has a low reversible thermal expansion, and many other good properties. Unfortunately it exhibits mechanical weakness, and for this reason has remained outside the range of potential structural materials. One example of the new type of structural carbon is Delanium, which depends for its strength on a single-phase structure and has good mechanical and thermal properties, while it can also be machined. Coking coal is very finely

ground, and to this small proportions of swell-inhibiting materials are added. The mixture is then pressed or extruded to desired form before firing in a controlled atmosphere, the temp cycle employed giving max shrinkage without distortion. The finished product has low porosity, and is mechanically strong. Different grades of carbon and their possible applications are described. A. S.

Distillation.

2131. Special slide rule speeds up distillation calculations. J. C. Chu, W. D. Robinson, and D. P. Doll. *Chem. Engng*, 1950, **57** (1), 108–9.—A simple four-scale slide rule and its use is described, which enables much more rapid solution of the Fenske equation and binary equilibrium data equations than by nomograph. D. H.

2132. Nomograph for the van Laar equation. J. C. Chu and C. C. Tung. *Chem. Engng Prog.*, 1950, **46** (1), 44–7.—A nomograph is presented for the prediction of vapour–liq equilibrium data using the van Laar equation. J. G. H.

2133. Evaluation of equilibrium stages and transfer units. K. O. Yu and J. Coull. *Chem. Engng Prog.*, 1950, **46** (2), 89–94.—A simplified method is presented for the calculation of the number of transfer units at finite reflux for systems with constant relative volatility in a packed fractionating column. Comparison with two existing correlations developed for plate columns reveals a close similarity. The precise relationship and analogy between plate and packed column are discussed. A simple type of equation is also developed, involving only two constants, to represent the vapour–liquid equilibrium relationship for many non-ideal systems. J. G. H.

2134. Flash equilibrium calculations: a modified rigorous method. C. F. Montross. *Chem. Engng Prog.*, 1950, **46** (2), 105–8.—The purpose of flash equilibrium calculations is described, and the use of the normal rigorous method is remarked. A modified method is presented which enables the E.P. to be fixed mathematically, and practical points in the calculation of flash equilibrium data are enumerated. J. G. H.

2135. Performance of drip-point grid tower packings. IV. Additional gas-film mass-transfer coefficients. L. J. Parsley, Jr., M. C. Molstad, H. Cress, and L. G. Bauer. *Chem. Engng Prog.*, 1950, **46** (1), 17–19.—Measurements of the rate of absorption of ammonia in water using the apparatus and 6295 Drip Point Grid packing described in previous papers are presented. The measurements were taken at six constant liquor rates using several gas rates for each.

The values so obtained are slightly more than twice those predicted by the Sherwood–Gilliland equation for wetted wall columns, the deviation being attributed to entrance turbulence. J. G. H.

2136. Performance of drip-point grid tower packings. V. Absorption of ethanol vapour. M. C. Molstad and S. F. Parlsey, Jr. *Chem. Engng Prog.*, 1950, **46** (1), 20–8.—Preceding papers have presented data on the performance of a single semi-plant packed column, employing several packings to determine liquid-film resistance and gas-film resistance. In an attempt to obtain additional data for systems in which major gas-film resistance is to be expected, ethanol vapour was employed, together with 6295 Drip-Point Grids, 1-in Raschig rings, and 1-in Berl saddles. Procedures adopted are described and results compared with those derived from the Sherwood–Gilliland equation. J. G. H.

2137. Solutropes. A. S. Smith. *Industr. Engng Chem.*, 1950, **42** (6), 1206–9.—A small number of ternary systems are known in which one component is distributed between two liquid phases in an apparent ratio varying with concn from <1 to >1. They are called solutropes, and their connexion with azeotropes is discussed. Such systems are believed to be regular solution compared to the majority of systems, the molecular

form in which the solute exists in the two solvents remaining unchanged between the extremes of concentration. Eleven systems, in which literature data show solutropy, are discussed. For seven of these the molecular-distribution constant was calc. The distribution equation yielding a constant between the extremes of concn of the distributed component is shown to be consistent with observed f. p. data. Relation of temp and distribution in solutropes is correlated by a van 't Hoff type equation.
R. G. T.

2138. Gasoline plant supplies naphtha for catalytic reforming. L. Dorsey. *Refiner*, 1950, **29** (4), 97–100.—A description of a gasoline plant processing natural gas from several fields. The plant produces propane, butane, 200-end point gasoline, naphtha, and kerosine. The 200–450° F naphtha cut is charged as feed stock to a catalytic reforming unit for production of premium motor gasoline. High- and low-pressure stripping stills are employed, and total condensation of propane is achieved at the high-pressure still overhead as a result of a demethanizer earlier in the flow.
R. W. G.

2139. Control point location and its effect on fractionator column operation. K. D. Uitti. *Petrol. Process.*, 1950 **5** (1), 41–4; *Refiner*, 1950, **29** (3), 130–4. (*Instrumentation Symposium, Texas A & M College, Oct.* 1949.)—The degree of purity to which a laboratory fractionating column separates the feed components was studied with respect to plate-temp conditions and optimum instrument-control position. With constant feed composition and varying reflux ratios the plate with max temp change is suggested as the optimum control point for reflux ratio or reboiler heat input. For a particular C_3–C_4 feed the middle plates of the stripping and rectifying sections both gave max temp changes, and instrumentation for rigid temp control at either of these points gave reasonable product purity control. Disadvantages are pointed out. For a fixed upper optimum plate temp and varying feed composition it was found that overhead was richer in C_3 for a low C_3 feed than for a feed richer in C_3, which is explained by means of McCabe–Thiele diagrams. The effect of holding a constant reflux rate is also considered.
D. W. F.

2140. Screen-skirted bubble caps. F. A. Zenz. *Refiner*, 1950, **29** (6), 103–5.—Simple experiments were carried out with air passing through a bubble cap immersed in water in a glass tank. By replacing the slots with an almost horizontal skirt of wire mesh the effective volume of liquid filled with rising air bubbles is increased. A further effect is that, whilst at low " vapour " velocities the pressure drop is slightly increased, at high velocities the pressure drop is less than that observed with the conventional bubble cap. An extended (or flared) prong-type cap has the same effect, but not to the same degree. From photographs it is estimated that the radius of bubbles from a screen-skirted cap is at least 30% smaller than the equivalent radius of a bubble formed at a slotted cap; hence an increase in efficiency is expected.
R. W. G.

Absorption and Adsorption.

2141. North Cowden gas injection project now in operation. N. H. Rahmes. *Oil Gas J.*, 20.7.50, **49** (11), 74.—Plant to increase ultimate oil recovery from the Grayburg formation and to permit the processing of all gas produced from the field has been put into operation at North Cowden field, Texas.

Plant processes 50,000 M.c.f. of gas/day, but by addition of compressors and heat exchangers this could be increased to 100,000 M.c.f/day, to produce propane, butane, and natural gasoline.

Field gas is gathered from 171 batteries, scrubbed and H_2S removed by mono-ethanolamine process. Discharge gas from fourth-stage compressors goes to well-injection system, whilst residue gas is subjected to absorption and distillation in conventional manner.

Tables show gas composition, daily production, and tower dimensions, and a flow sheet is given.
G. A. C.

2142. New Burnell–N. Pettus cycling plant recovers 330,000 gals/day of liquids. D. P. Thornton. *Petrol. Process.*, 1950, **5** (5), 477–82.—One of the largest gas-cycling plants constructed in the southwestern states, recently completed in Texas is described. It processes gas from the Burnell and N. Pettus condensate fields and casinghead gas from surrounding crude-oil wells, brought to the plant through nineteen gathering lines at well-head pressure. It is operated by the Stanolind Oil & Gas Co., for themselves and twenty-odd other joint owners. Designed capacity is 194,000 M.c.f./day gas, recovering over 330,000 gal/day of liquid products ranging from propane to finished motor fuel and kerosine. The condensate and casinghead gas are handled by two separate systems, while the distillate is processed separately from the rich oil. Other points of interest include the mid-section pump around circuit through a fired heater for process heat in the primary still; a " propanizing " absorber on the recycle-gas stream recovering C_3+ components with a rich oil which is partially stripped of methane and ethane, minimizing lean-oil circulation. Plant utilities are well covered. D. W. F.

2143. Gas conservation by repressuring, natural gasoline recovery and fuel use. A. L. Foster. *Petrol. Engr*, Jan. 1950, **22** (1), C-21.—The Silsbee, Texas, natural gasoline and re-pressuring plant is part of the gas-conservation programme. Having a capacity of 55 M. cu. ft. of gas/day, the plant has six streams at different pressures, and the plant layout and flow sheets are given to show how these streams are handled. The various streams are 35 M. cu. ft/day of distillate gas. The residue gas from this is used for re-pressuring; 12 M. cu. ft/day of flare gas from refineries and 7½ million from minor sands. Products are gas for re-pressuring, pipeline gas, low-pressure gas, propane, natural gasoline, and kerosine. Tables are given of the analyses of the inlet and outlet gas streams. G. K. A.

2144. Absorption in packed towers. R. W. Houston and C. A. Walker. *Industr. Engng Chem*, 1950, **42** (6), 1105–12. (*Symposium on absorption and extraction, Divn of Industr. & Engng Chem. 116th annual symposium, Amer. Chem. Soc., Ohio.*)—Data are presented on the effect of gas diffusivities on the rate of absorption of acetone, ethanol, methanol, and ammonia from air into water in a 12-in-dia column packed to 2 ft with 1-in Raschig rings. The gas rates used were 600 lb/hr ft² since it was explained that above this the method of calculation was inaccurate. Overall mass transfer coefficients were calculated, and individual coefficients derived by the Sherwood and Holloway relation involving Henry's Law (*Trans. Amer. Inst. chem. Engrs*, 1940, **36**, 21, 39) $k_g a$ was found to vary as the $\frac{2}{3}$ power of diffusivity from $L = 500$ to 2000 lb/ft² hr. Above this it was independent unless the data on ammonia was ignored on the grounds of anomalous and complex behaviour. It is pointed out that the correlation with diffusivity is empirical, and has no basis in theory when conditions involve eddy diffusion. The authors conclude that having only four points, and using different analytical techniques for each, may lead to erroneous comparisons.

D. H.

2145. Effect of diffusivity on gas film absorption coefficients in packed towers. A. E. Surosky and B. F. Dodge. *Industr. Engng Chem.*, 1950, **42** (6), 1112–20. (*Symposium on absorption and extraction. Divn of Industr. & Engng Chem. 116th annual symposium, Amer. Chem. Soc., Ohio.*)—The effect of molecular diffusivity on the rate of mass transfer was found to be very small. In this investigation the exponent of 0·15 was found to correlate the results, and compared well with the figure 0·17 found by Mehta and Parekh for ½-in Raschig rings.

The systems used were water, methanol, benzene, and ethyl *n*-butyrate absorbed from a stream of dried air (140–500 lb/hr ft²) by water (435–5000 lb/hr ft²) in an 8-in-outside-dia tower packed with 1-in carbon rings to heights between 4 and 12 in. Gas pressure of 1 atm and temp 5–24° C maintained throughout.

The results from existing literature are criticized and their accuracy discussed. Studies on absorption and vaporization with a given system under varying pressure are recommended, since $D \propto 1/p$. Further results from variation of the carrier gas might throw light on the dependence on diffusivity. D. H.

2146. Liquid-gas interfacial area in packed columns. J. Weisman and C. F. Bonilla. *Industr. Engng Chem.*, 1950, **42** (6), 1099–105. (*Symposium on absorption and extraction, Divn of Industr. & Engng Chem., 116th annual symposium Amer. Chem. Soc., Ohio.*)—The proportion of wetted packing to total packing surface is calculated by comparing H.T.U. values for the evaporation of water into air on normal non-porous packing with those on a completely wetted packing as found by Gamson *et al* (*Trans. Amer. Inst. chem. Engrs*, 1943, **39**, 1). Results for mass transfer varied from 4 to 25%, and for heat transfer from 13 to 42%. The tower was 8 in high and 4 in dia with headers above and below for liquid distribution and gas–liquid separation. To eliminate these end effects, the transfer units of 5 in height and 8 in height were subtracted. Brass and glass spheres 0·50 in dia were used, but no difference was detected. Graphs, drawn by eye, through the results have the following equations :—

Packed height.

8 in	$N_d = 0{\cdot}077\ (L)^{0{\cdot}5}\ (Re)^{-0{\cdot}1}$
8 in	$N_h = 1{\cdot}77\ \ (L)^{0{\cdot}3}\ (Re)^{-0{\cdot}25}$
8 in	$N_d = 0{\cdot}058\ (L)^{0{\cdot}5}\ (Re)^{-0{\cdot}1}$
5 in	$N_h = 1{\cdot}40\ \ (L)^{0{\cdot}3}\ (Re)^{-0{\cdot}25}$

Similar calculations are made for Raschig rings from the data of Taecker and Hougen (*Chem. Engng Progress*, 1949, **45**, 188) and McAdams (*Chem. Engng Progress*, 1949, **45**, 241). They give very similar graphs, but with effective areas from 40 to 80% of the total. D. H.

2147. Theoretical analysis of fractionating process of adsorption. B. J. Mair, J. W. Westhaver, and F. D. Rossini. *Industr. Engng Chem.*, 1950, **42** (6), 1279–86. (*Adsorption Symposium, Divn of Petrol Chem. and others. 116th Mtng Amer. Chem. Soc. Atlantic City, N.J., Sept.* 1949.)—A theoretical study is made of the fractionating process of adsorption on the basis of the concepts used in theoretical analysis of fractionating processes, *e.g.*, distillation. Equations are developed to determine the separation factor for binary solutions and the height equivalent of unit theoretical stage of separation. The separation factor is determined experimentally for benzene with each of the following : *n*-propylbenzene, ethylbenzene, *n*-hexane, and *cyclo*hexane, and is expressed as a function of concn of these solutions. Experimental determination of the height equivalent to unit theoretical stage is made for the first three of the above solutions. R. G. T.

2148. Liquid phase adsorption equilibria and kinetics. S. Eagle and S. W. Scott. *Industr. Engng Chem.*, 1950, **42** (6), 1287–94. (*Absorption Symposium. Divn of Petrol Chem. and Others.—116th Mtng Amer. Chem. Soc., Atlantic City, N.J., Sept.* 1949.)—Simple experimental methods are described for measurement of equilibria and rate processes involved in liquid-phase adsorption. Isotherms, equilibrium diagrams, adsorptive capacities, diffusion coeffs, and fracture resistance of various adsorbents are given. The toluene-*iso*-octane system has been found useful for comparison of selectivity, diffusivity, and fracture resistance of adsorbents used in petroleum refining–silica, silica–alumina, and charcoal. Effect of heat pre-treatment on absorbent properties and kinetics is briefly described. R. G. T.

2149. Countercurrent flow of particles through moving continuous fluid. Pressure drop and flooding in spray-type liquid towers. J. C. Elgin and H. C. Foust. *Industr. Engng Chem.*, 1950, **42** (6), 1127–41. (*Absorption and Extraction Symposium, Divn of Industr. Engng Chem., Amer. Chem. Soc., Ohio State Univ. Dec.* 1949.)—Basic relationships of liquid, gas, and solid phases in spray towers and the relation of solid phases to a fluidized bed of solids are discussed. Assuming that in a spray tower and fluidized bed operational factors and relation between void fraction and modified Reynold's number are identical, the authors develop equations to predict pressure drop for spherical particles in spray towers. Pressure drop and flooding-velocity data, obtained in a solids–liquid spray tower with two liquids and three particle sizes, have been expressed as functions of solids and liquid-flow rate. Data agree well with pressure drop according to theory advanced. Flooding-velocity data and liquid–liquid data are also correlated by graphs, of K_p vs Re_0 and of slip velocity vs D_p. The latter is suggested as a reasonable approx for general use. R. G. T.

2150. Mass transfer of pure liquids from a plane, free surface. L. J. O'Brien and L. F. Stutzman, *Industr. Engng Chem.*, 1950, **42** (6), 1181–7. (*Symposium on Absorption and Extraction. Divn of Industr. & Engng Chem. 116th annual symposium Amer. Chem. Soc., Ohio.*)—Vaporization data on acetone, benzene l-propanol, toluene, and water from a plane, immobile, free surface to a laminar or turbulent stream of air across the surface were correlated by the empirical equations :—

$$(1)\ \text{kg} \cdot P_{BM} = 0{\cdot}041 D^{1{\cdot}1} G^{h},$$

where $h = 0{\cdot}54/D^{0{\cdot}3}$

$$(2)\ \frac{d}{x} = 0{\cdot}20 \left(\frac{\mu}{D}\right)^{-1{\cdot}2} \left(\frac{dup}{\mu}\right)^{b},$$

where $b = 0{\cdot}63 \left(\frac{\mu}{D}\right)^{0{\cdot}3}$.

Average deviations were 4%. It was found impossible to correlate all systems by simple functions of the diffusivity or the Schmidt group. The equations were modified to correlate existing data from similar apparatus, and other equations involving the J-factor give similar accuracy. D. H.

2151. Gas-bubble columns for gas liquid contacting. H. L. Shulman and M. C. Molstad. *Industr. Engng Chem.*, 1950, **42** (6), 1058–70. (*Absorption and Extraction Symposium. Divn of Industr. Engng Chem., Amer. Chem. Soc., Ohio State University, Dec.* 1949.)—Pressure drop and liquid-film mass-transfer characteristics have been determined for absorption columns, in which bubbles, formed by passing a gas through a porous plate, rise in a descending continuous liquid phase. Mass-transfer rate is shown to be a function of gas rate in the streamline region but not in the turbulent region. In both regions rate of mass transfer is shown to be a function of liquid rate, water temp, column height, and liquid diffusivity. Mass-transfer rate does not depend on column dia, plate porosity, or direction of mass transfer. Three empirical equations are developed to correlate the data—two being for the streamline region.

It is concluded that gas-bubble columns exhibit mass-transfer rates of similar size to packed columns, at low liquid rates. At high liquid rates where packed columns are inefficient, gas-bubble columns show greater mass-transfer rates. In comparing the two types of columns the greater pressure drop across the gas-bubble column must be taken into account. R. G. T.

2152. Stagewise absorption and extraction equipment. Transient and unsteady state operation. L. Lapidus and N. R. Amundson. *Industr. Engng Chem.*, 1950, **42** (6), 1071–8. (*Absorption and Extraction Symposium. Divn of Industr Engng Chem., Amer. Chem. Soc., Ohio State University, Dec.* 1949.)—A theoretical investigation is made into the transient and unsteady state behaviours of stagewise absorption and extraction equipment, both cross-current and countercurrent. A plate-type absorber is assumed to be fed with a fat gas stream and lean oil stream at constant inert rate. Compositions of the streams are functions of the time, and any arbitrary composition can exist initially on the plates. Equations are developed to show the variation of composition of both streams with time, a linear equilibrium relation being assumed between the two phases. Computation of composition on any plate at any time is then possible. Two numerical examples are given which, in addition to composition variation, indicate the time necessary to reach equilibrium when the unit is upset by feed stream variations. Methods of solution given here are applicable to other stagewise problems, *e.g.*, distillation and purging of chemical reaction systems. R. G. T.

2153. Semicommercial multistage extraction columns. Performance characteristics. E. G. Scheibel and A. E. Kerr. *Industr. Engng Chem.*, 1950, **42** (6), 1048–57. (*Absorption and Extraction Symposium, Divn of Industr. Engng Chem., Amer. Chem. Soc., Ohio State University, Dec.* 1949.)—Performance characteristics of a 12-in multistage extraction column have been investigated using systems including acetone–*o*-xylene–water, acetic acid–*o*-xylene–water, and acetic acid–methyl *iso*butyl ketone–water. Increase of agitator speed and of liquid throughput are both found to increase stage efficiency up to a max and then, in some cases, decrease it before flooding occurs. This phenomena is discussed. Solvent properties are shown to affect performance—high

solvent ratios can be used for a given performance, but high agitator speeds are then required. Optimum packing height for various solvent pairs agreed with previous results on a 1-in laboratory column. Effects of other factors in column design are considered. Packing characteristics affect efficiency. Column capacity depends on solution used (350–600 gal/hr/sq. ft. of cross-section). Theoretical stage was 9–16 in under optimum conditions—similar to theoretical stage height of more efficient distillation-column packings. R. G. T.

Solvent Extraction and Dewaxing.

2154. Commercial extraction equipment. V. S. Morello and N. Poffenberger. *Industr. Engng Chem.*, 1950, **42** (6), 1021–35. (*Absorption and Extraction Symposium. Divn. of Industr. Engng Chem. Amer. Chem. Soc., Ohio State University, Dec.* 1949.)—Summary is made of contemporary data on commercial extraction equipment. Major applications of liquid–liquid extraction processes and general design considerations are described. Performance characteristics of forty-seven extractors are tabulated and briefly described. Film-type extractors, spray towers, baffle towers, perforated plate columns, bubble-cap columns, packed-tower extractors, and centrifugal extractors are included. Extensive bibliography is appended. R. G. T.

2155. Temperature studies in packed liquid–liquid extraction tower. V. S. Morello and R. B. Beckmann. *Industr. Engng Chem.*, 1950, **42** (6), 1078–87. (*Absorption and Extraction Symposium. Divn of Industr. Engng Chem., Amer. Chem. Soc., Ohio State University, Dec.* 1949.)—Effect of temp on mass transfer was studied in a $1\frac{3}{4}$-in-dia counter-current, liquid–liquid extraction column packed with 53 in of 4-mm glass beads. Extraction of diethylamine from water by toluene was performed at 26·8°, 38·5°, 48·5°, and 57·5° C. Individual film-transfer units were estimated. H_t value of the water film was nearly zero. H_t value of toluene film decreased with temp increase according to :—

$$(H_t)_T = 1{\cdot}81 - 1{\cdot}498 \times 10^{-6} t^{3{\cdot}2} \ (t \text{ being temp } ^\circ\text{C})$$

Fine packing, wetted solely by continuous phase, shows high efficiency, since coalescence is prevented and a large interfacial area of contact between the two phases is maintained. Under constant interfacial area at all flow conditions and temp $(H_t)_T$ showed a variation with temp that was power function of the Schmidt number $\mu/\rho D$:—

$$(H_t)_T = 1{\cdot}97 - 0{\cdot}91 \times 10^{-6}/(\mu/\rho D)^{2{\cdot}78}$$

R. G. T.

2156. Solvent extraction of tar acids from coal tar hydrocarbons. C. F. Prutton, T. J. Walsh, and A. M. Desai. *Industr. Engng Chem.*, 1950, **42** (6), 1210–17.—Extraction studies with methanol–water mixtures as solvents for various hydrocarbons and phenols found in coal tar are described. Solubility data at 10°, 25°, and 35° C are given. Solutes were phenol, *p*-cresol, 2-naphthol, *p-tert*-butylphenol, methyl naphthalene, hexadecane, and 2 : 2 : 4-trimethylpentane. R. G. T.

2157. Toluene extraction from petroleum with water solutions. G. B. Arnold and C. A. Coghlan. *Industr. Engng Chem.*, 1950, **42** (6) 1217–22.—Batch studies on the recovery of toluene from toluene concentrates of hydroformed naphtha by extraction with 20% aqueous solution of ammonia and 25% aqueous solution of ethylene glycol at temp near 300° C. Use of ammonia and ethylene glycol is shown to effect reduction in solvent dosage and/or number of stages required with water as solvent. A lower extraction temp and pressure may be used with ethylene gylcol solution, but increased recycle ratio necessitates the same solvent dosage. Use of ammonia reduces the extraction temp, but not the extraction pressure, because the ammonia exerts a high vapour pressure. R. G. T.

2158. Mass transfer from packing to organic solvents in single phase flow through a column.—B. F. Gaffney and T. B. Drew. *Industr. Engng Chem.*, 1950, **42** (6), 1120–7.—Mass-transfer coefficients for three organic solvents (acetone, benzene, and *n*-butyl

alcohol) flowing through a bed of $\frac{1}{4}$-, $\frac{3}{4}$-, and $\frac{1}{2}$-in pellets of succinic and salicylic acids in a 3 in-dia column were determined. All physical constants involved were determined experimentally. Plots of the results show that aH_t (interfacial area between dissolving solid and solution per unit volume of solid bed × height of transfer unit) increased with the 0·58 power of the Schmidt number, whereas the earlier reports of Hunt, Wilke, and Hougen on transfer to gas chose the $\frac{2}{3}$ power. aH_t was also shown to increase with increased modified Reynold's number, and this rate fell off with increasing Reynold's number. Modified Reynold's numbers were varied from 0·8 to 1500, and Schmidt numbers from 150 to 13,000. Free convection within the solid bed in some cases caused adverse effects by raising the inlet-solvent concentration. It is pointed out that this phenomena might be present in extraction and catalysis.

R. W. G.

Cracking.

2159. World's largest " cat " cracker.—Anon. *Petroleum*, Apr. 1950, **13** (4), 92–3.—Designed to meet increased demand of petrol and heating oil, the Esso Standard Oil Co. has completed a major expansion of its Bayway refinery at Linden, New Jersey.

It includes installation of a 49,000-b.d. vacuum pipe still which receives residual oil and prepares from it a feed stock for a new 41,000-b.d. fluid catalytic cracking unit. The still is designed to minimize the Conradson carbon and ash contents of the flashed distillate products, as these are detrimental to the fluid catalyst used.

The cat cracker is of tremendous size, but is very simple, consisting of two main vessels, reactor and regenerator, side-by-side, thus reducing the overall height; a fractionator, and other accessories. Cyclone collectors are used to remove entrained catalyst particles from cracked vapours and flue gases.

The engineering and operation of the plant are described. R. E. P.

2160. Catalytic cracking, Part I. M. Sittig. *Refiner*, 1950, **29** (6), 91–5.—A review of catalytic cracking, mentioning the early McAfee process, but being mainly concerned with the developments of the Houdry processes. The method of action of various catalysts is reviewed and the economics of catalytic cracking considered. Article is concerned with the production of gasoline, and both cracking and reforming are mentioned. R. W. G.

2161. Catalyst fluidization. Anon. *Fluid Handling*, Jan. 1950 (2), 7–9.—Four main features of the thermofor catalytic cracking process have been modified, and it has been given the name Houdriflow. The bucket elevator for catalyst pellets is replaced by flue-gas lift. This simplification enables the catalyst to circulate faster, and is more flexible. Consequently, catalyst-to-oil ratios are doubled, and sensible heat of the catalyst reduces the need for feed heating. It also allows the number of burning zones in the regeneration to be reduced from seven to two. The reactor and regenerator are built together in one tower, reducing the space occupied by the plant and eliminating one of the catalyst lifts.

Economic advantages are stated to be 20% saving in capital investment and lower running and maintenance costs. D. H.

2162. Cracking unit yield is raised by improved vapour removal. Anon. *Petrol. Process.*, 1950, **5** (5), 519.—An improvement in olefin and acetylene yield by re-design of the vapour-removal system for a cracking reactor is claimed in U.S.P. 2,000,870, an illustration of which is included in this review. A much smaller than conventional vapour space is used above the catalyst or pebble bed, thus reducing vapour-retention time in the heater. This is achieved by a series of outlets in the top of the reactor leading into Venturi tubes, ejector operation being obtained by an atomized water-quench injection. D. W. F.

2163. Performance of thermal poly trans-economizers. J. H. Smith. *Oil Gas J.*, 3.8.50, **49** (13), 45.—In 1946 a catalytic polymerization unit was added for processing the propane–butane fraction recovered from the thermal cracking and reforming plant installed at the Wichita Falls refinery of the Continental Oil Company, U.S.A.

The flow sheet shows that the furnace feed pump discharges via a cooler through

trans-economizers into the furnace coil, charge being heated to about 1000° F at 1500 p.s.i.g., then held in convection soaking tubes during which the reaction takes place. The furnace effluent flows into a partial stabilizer after passing through the trans-economizers, which latter consist of six 40-ft shells in series, each shell being of 4·4 in internal dia and containing 4½ in outside-dia tubes. A figure gives a day-by-day plot of the heat-transfer coefficient obtained when the unit was operating on an essentially butane feed, and a summary of the run is discussed. It is concluded that the trans-economizer system is simpler in design and lower in construction and operating costs than one involving a tar knock-out drum and circulating quench, and waste-heat recovery at a higher temperature level is made possible. G. A. C.

2164. Platforming. V. Haensel. *Refiner*, 1950, **29** (4), 131–6. (*Western Petroleum Refiners' Assoc. Mtng, San Antonio, U.S.A.*)—A detailed discussion of the reforming process for straight-run and natural gasolines in the presence of hydrogen using a platinum catalyst. The chief reactions involved are the conversion of naphthenes to aromatics and hydrocracking of high-molecular-weight paraffins. Relatively low-temp conditions are used (less than 900° F) which, with the presence of hydrogen, do not lead to carbon formation. Thus, catalyst does not require regeneration while the plant is on stream. Platforming may be carried out with advantage on heavy products of thermal cracking and reforming. Product of platforming suffers marked increase in octane rating, *e.g.*, 52·8–94·3 (Research F-1 + 3 c.c. T.E.L.) and reduction in sulphur content (about 96% reduction on charge). Vol yield is of the order of 95%, and the product stores free from gum formation without the need for inhibitors. During four months' operation of the platforming plant installed by the Old Dutch Refinery in October 1949 the catalyst has given no indication of deactivation. Operating costs are low, owing to the absence of catalyst regeneration and of product re-running.
R. W. G.

Polymerization.

2165. Effect of alternating electrical fields on the polymerization of styrene. W. A. Bryce, C. A. Genge, and C. A. Winkler. *Canad. J. Res.*, 1950, **28**, 117–31.—The apparatus for studying the effects of alternating fields on chemical reactions, with careful account being taken of temp charges caused by dielectric heating, is described.

The four variables—field, frequency, reaction temp, field strength, and cat concentration—were considered in the polymerization of liquid styrene. Cat concentration was varied, using field strengths of 1500–4500 V/cm at 1·55 M.c. Temp and V were varied at three cat concentrations and const frequency. Frequency ranges from 1·15 to 7·72 Mc., were used at const V, cat concentration, and temp. At all temperatures, cat concentration, V, and frequencies the fields had no significant effect on the visc average mol. wt. of the polymer. By the application of the fields the rate of polymerization was reduced; the inhibition was shown to vary as the 1·8th power of the voltage.

Fields of 4500 V/cm appeared to reduce the activation energy for the benzoyl-peroxide-catalysed polymerization by 50%, although the change is only slight at 3000 V. Variation of frequency over the above range does not significantly affect the percentage conversion. The fields appear to have a greater inhibiting effect on the oxygen-catalysed than on the benzoyl-peroxide-catalysed reaction. N. T.

Alkylation.

2166. Propylene, a valuable feed stock for alkylation. E. C. Oden, W. J. Burch, Jr., and G. R. Jones. *Refiner*, 1950, **29** (4), 103–8.—A description of the alkylation process, incorporating propane–propylene feed, at the Cites Service Tutwiler Refinery, Lake Charles, La., U.S.A. Comments and a flow diagram with several operating conditions are given. 87–93% H_2SO_4 is used as catalyst, and the ratio of *iso*butane to olefins in the inlet streams to the reactors is approximately 6 : 1. The *iso*butane-to-olefin ratio within the reactors is approx 115 : 1, and the acid-to-hydrocarbon ratio held at 1 : 1. Reactors run at 45–75° F with a contact time of 20–35 min. Comparisons are given between propylene and butylene alkylates and for alkylate made from mixtures of the two. Due to its low 50% point, propylene alkylate is considered a better

motor gasoline blending stock than butylene alkylate, although its A.S.T.M. octane rating is slightly lower. Owing to octane rating, butylene alkylate is preferred for high-quality aviation spirit. R. W. G.

Isomerization.

2167. The *cis trans* isomerization of azobenzene in solution. J. Halpen, G. W. Brady, and C. A. Winkler. *Canad. J. Res.*, 1950, **28**, 140–55.—Using existing theories of solution and of chemical kinetics, relations for the solvent effect on unimolecular, non-ionic reactions are derived. The activation energy is linearly related to $(Ps^1)^{\frac{1}{2}}$, where Ps^1 is the internal pressure of the solvent. The frequency factor of reaction, A, in the form of log A is linearly related to the activation energy, and the combination of these two relationships with the Arrhenius equation gives a linear relation between log of specific rate constant for the reaction and $(Ps^1)^{\frac{1}{2}}$ for the reaction in different solvents. To test this equation the kinetics of the *cis trans* isomerization of azobenzene in various solutions were studied. The two isomers were analysed by a Beckman spectrophotometer. The activation energy and the frequency factor were calculated for the reaction in sixteen pure solvents.

The experimental results show the above relationship to hold for this reaction; deviations being more marked in polar solvents. In highly polar solvents the deviation from the linear plot is considerable. The kinetics of reaction in mixed solvents seem to show that the azobenzene molecules are surrounded by molecules of the component in which it is most soluble. N. T.

Chemical and Physical Refining.

2168. Gaylor caustic recovery process. Anon. *Refiner*, 1950, **29** (6), 119.—Spent caustic obtained during the sweetening of sour naphthas and similar products is passed to an electrolyser where the nascent oxygen liberated reacts with mercaptans to form disulphides which separate as an oily layer. The regenerated caustic can then be returned to the scrubbing-tower. 0·6 lb of sulphur are removed per kW.hr. R. W. G.

2169. Skelly removes H_2S from sour gas at Eunice. Anon. *Refiner*, 1950, **29** (1), 135.—A diethanolamine gas-sweetening unit as applied to casinghead gas is described and a flow diagram given. The natural gasoline obtained from the sweetened gas requires no treatment except washing with caustic to remove mercaptan sulphur to prepare it for fractionation and shipment. R. W. G.

2170. Separation of gases by fractional permeation through membranes. S. Weller and W. A. Steiner. *J. appl. Phys.*, 1950, **21** (4), 279–83.—The permeability of a number of thin organic films towards oxygen and nitrogen has been measured. Using an ethyl cellulose film these studies were extended to include carbon dioxide, argon, helium, and nitrogen. The enrichment of a binary gas mixture in a single stage of permeation has been calc for the extreme cases of perfect mixing and no mixing. A fractional permeation process may be of use in effecting the separation of oxygen from air, helium from natural gas, hydrogen from coke-oven gas, and of hydrogen from tail gases of various hydrogenation processes. D. F. J.

2171. Mathematics of adsorption in beds. II. N. R. Amundson. *J. Phys. & Colloid Chem.*, 1950, **54** (6), 812–20.—Equations are developed which cover adsorption and desorption in beds. The bed may have arbitrary distribution of adsorbate on it, and the inlet solution conc may have an arbitrary dependence upon time. The equations are developed for the cases of two different mechanisms controlling in the bed. No simplifying assumptions are made; the solutions are therefore mathematically exact for the cases considered. D. F. J.

2172. Mathematics of adsorption in beds. III. Radial flow. L. Lapidus and N. R. Amundson. *J. Phys. & Colloid Chem.*, 1950, **54** (6), 821–9.—Equations for single-solute radial-flow adsorption are derived and solutions obtained for the two cases of equilibrium and non-equilibrium. In the first case, the solution is obtained by the

use of the La Place transformation for a linear isotherm, and in the second, a kinetic equation of the Langmuir type is assumed. D. F. J.

2173. Adsorption–desorption hysteresis in relation to capillarity of adsorbents. C. Pierce and R. N. Smith. *J. Phys. & Colloid Chem.*, 1950, **54** (6), 784–94.—Evidence is presented which indicates that desorption hysteresis does not require prior capillary condensation, but may occur when adsorbate is held on a plane surface. In this case adsorption occurs by the merging of clumps of molecules on separate sites. As the forces holding the molecules are stronger after merging than before, the vapour pressure is lower and desorption hysteresis occurs. The most common case of hysteresis is when capillaries are filled by the meeting of multilayer films on opposite walls. Small capillaries may fill by condensation, which starts at the narrowest places. The absorbed layer does not then change as adsorption proceeds, and there is no hysteresis. Criteria are suggested for the recognition of capillary condensation in adsorption.

Pore-size computation is discussed with particular reference to the applicability of the Kelvin equation. It is concluded that there is no reliable method for this determination.

The phenomena observed when scanning a hysteresis loop are considered in the light of the theory. D. F. J.

2174. Heats of adsorption. IV. Entropy changes in adsorption. C. Pierce and R. N. Smith, *J. Phys. & Colloid Chem.*, 1950, **54** (6), 795–803.—Entropy changes for adsorption processes have been computed by the relation $T\Delta S = H - \Delta P$. The curve of $T\Delta S$ against relative pressure has been observed for a variety of systems, including butane on glass spheres, and benzene and *cyclo*hexane on Graphon. The curve shows three regions: an entropy increase as the first molecules are adsorbed in a disorderly array, an entropy decrease as the surface becomes covered with a monolayer and the molecules arrange themselves in an orderly manner, and a small entropy decrease in the region of multilayer adsorption which approaches zero as p approaches p_o.

An interpretation is suggested for the isotherm of water on a plane carbon surface. The limitations which may apply to the use of the Clapeyon equation for computing heats of adsorption are discussed. D. F. J.

2175. Skid-mounted gas-dehydration plant. L. H. Peahl. *Oil Gas J.*, 13.7.50, **49** (10), 92.—Installation, operation, and performance of a skid-mounted gas-dehydration plant employing triethylene glycol as the liquid absorbent are described.

Plant is operated by Southern California Gas Co. at Kettleman Hills, and can process 25 M.M.c.f. of gas per day.

Wet gas enters at base of contact tower, treated with counter flow of glycol. Water-rich glycol removed and re-concentrated. Water-lean glycol from reboiler flows back via storage tank to tower. Dry gas leaves at top of contact tower, water vapour passes off at top of still.

A summary of operating data is given. G. A. C.

2176. Neutralization of spent caustic with flue gas. K. M. Brown and S. Kurtis. *Oil Gas J.*, 20.7.50, **49** (11), 81.—The different refining operations in which caustic solutions are used will result in different objectionable compounds being present in the waste liquor. For example, sulphides and mercaptides will be present in caustic used for treating light, straight-run gasoline, but that used for treatment of thermally cracked gasoline may contain in addition phenolates, thiophenolates, and salts of naphthenic and aliphatic acids.

Aurora Gasoline Co. passed hot flue gas from the downstream side of the catalytic-cracking-unit waste-heat boiler upward through a vertical tower which contained carbon Raschig ring packing. Flue gas from top of tower passed directly into a boiler fire-box. Steam injection prevented excessive evaporation, thus avoiding dehydration and preventing caustic concentration getting into range where caustic embrittlement would become a problem. Efficiency was found to be about 50%. Flow sheets of the unit are given, and tables show comparison of strength of acids and bases, and acidity of sodium salts of certain acids occurring in unfinished petroleum products. G. A. C.

2177. Filter performance trebled. J. A. Pickard. *Fluid Handling*, Jan. 1950 (2), 13–16.—An apparatus for the batch addition of filter aids to aqueous liquids is described. It is stated that fluctuations in the ratio of solid to liquid are less than in other systems, and there is no tendency to carry coarser particles on first.

The vertical limb of an inverted T-piece carries an axial partition, causing the liquid to flow up one side and down the other. Above the turbulent region of the top of the partition a plug cock adjusts the flow of solids from a conical hopper. D. H.

2178. Re-refining used aircraft oils. Anon. *Petroleum*, May 1950, **13** (5), 119.—85,000 gal of oil have been salvaged, and some 40,000 gal of petroleum solvents have been reclaimed in one year by American airlines using a Refinoil unit. Used lubricating oil is mixed with activated earth and drawn by vacuum into an electrically heated still, where moisture and diluents are stripped off. After this the oil and earth flow by gravity to a contact tank, where a filter aid is added, and then the mixture is pumped through a filter-press. Re-refined oils are shown by laboratory tests to be equal to new oils, except for bearing corrosion. In service, no difference is noted as regards corrosion. R. E. P.

Special Processes.

2179. Stanlow carbon black plant. Anon. *India Rubber J.*, 1950, **119** (6), 216.—A description is given of the opening of the new £500,000 20-acre Cabot plant, to which heavy petroleum residues, the raw material for carbon-black production, will be delivered by pipeline from tankers in the Manchester Ship Canal. Initially the raw material will be of U.S. origin, as suitable British products are not at present available in the required quantities. Some economic aspects are considered. C. N. T.

2180. Richardson's experimental carbon black hot house. E. J. Claasen. *India Rubber World*, 1950, **122** (3), 313.—A description is given of an experimental pilot plant for the production of channel-type carbon black, in which new plant-operating conditions are investigated. Two identical test sections are used, one for the study of the effects on yield of uncontrollable variables, and the other for the investigation of the influence of controllable variables. C. N. T.

2181. Simplicity and efficiency mark grease plant design. A. L. Foster. *Petrol Engr*, Dec. 1949, **21** (13), C-24.—The plant is set in a four-storey building, the fourth storey containing working storage tanks for oil and fatty acid. On the third floor are ten grease kettles of 1700 gal capacity, an experimental kettle, and two pressure soap kettles of 300 gal capacity. One soap kettle is connected to four grease kettles. All have double-action mixing paddles and side scrapers. On the second floor pumps at the base of the kettles feed the product to automatic can-filling machines or to the drum-filling machines on the first floor. Greases requiring milling are cooled for 24 hr before passing through the milling machine. At the plant is provided a drum-reconditioning unit, drum storage, and rail- and ship-loading facilities. G. K. A.

2182. Continuous manufacture of grease. H. E. Bloomsberg and A. Beerbower. *Petroleum*, May 1950, **13** (5), 115–18.—Continuous blending of soap base and lubricating oil appears to offer greater efficiency, with lower manufacturing costs, than manufacture by the kettle method. The process depends on the fact that calcium-grease bases are semi-plastic above 200° F and can be pumped with lubricating oil and water to produce grease by turbulent mixing with hot oil in a centrifugal pump. The process consists of three basic steps: (1) semi-continuous manufacture of calcium-grease base, which requires less time for saponification, and less soap than does the kettle method, to meet given finished grease specifications; (2) oil storage and blending; (3) continuous oil blending with the base using a Lancaster disperser, employing a turbine-rotor-mixing principle.

A continuous viscometer for consistency control and equipment for packaging of finished greases and for continuous blending of extreme-pressure lubricants are described. Excellent quality greases from No. 00 to No. 4 N.L.G.I. classifications are obtained, but kettle production of other grades is preferred, since demand is relatively small. R. E. P.

Metering and Control.

2183. Simple method of producing thermocouple junctions. K. F. Hager, M. Rosenthal, and W. Ross. *Oil Gas J.*, 13.7.50, **49** (10), 87.—The method consists of welding by heat from an arc formed at the moment of contact between the thermocouple junction to be welded and an oil-covered mercury surface. The mercury and the thermocouple wires are connected to opposite poles of a source of current.

Available wattage, dimension, composition, and resistance of wire must all be taken into account to produce a satisfactory weld. G. A. C.

2184. Some fundamentals of temperature measurements with thermocouples. G. L. Farrar and A. M. Platt. *Petrol. Engr*, Dec. 1949, **21** (13), C-5.—The e.m.f. produced by a thermocouple is the sum of the Peltier e.m.f., produced by the junction of two dissimilar wires, and the Thomson e.m.f., the potential which exists in a homogeneous wire having a temperature gradient. The e.m.f. characteristics compared with platinum are given in a chart. At the hot junction the wires are fused together, and provided the end is at a uniform temp the presence of any other metal has no effect. Thermocouples may be connected in series to amplify the e.m.f. or in parallel when an average temp is recorded. To measure the e.m.f. produced a millivoltmeter or some type of potentiometer is used. A millivoltmeter requires a current, and so is subject to the error due to the resistance of the leads and thermocouple and so requires calibrating for each system used. Diagrams are given of potentiometer circuits. One source of error at the thermocouple hot junction is the transient heat transfer lag caused by a sudden change of temp. This can be calculated from Newton's law of cooling. Another error is the steady state heat transfer lag due to the temp gradient from the hot material through the thermocouple to the outside. For gas temperatures of 1200–2000° F this latter error may be 100–600° F. G. K. A.

2185. Measurement of high temperatures in gas streams. A. I. Dahl. *Refiner*, 1950, **29** (3), 115–22.—Accurate temp measurement is of fundamental importance in many industrial processes. The accuracy obtained depends upon how closely the sensitive element of the measuring device (*e.g.*, a thermocouple junction) is brought to the same temp as that of the object or space. With high-temp gases this is not easily achieved. If the gas is not in thermal equilibrium with its surroundings (*e.g.*, hot exhaust gas in an uninsulated pipe) and a bare thermocouple is inserted, then the temp attained by the couple will be such that the heat received by convection is equal to the heat lost to the walls by radiation and conduction. Conduction effects can be reduced by increased depth of immersion and suitable insulators. Radiation effects are the primary source of uncertainty with temps of 1000° F and above. This effect is reduced by small-dia wires and by coating thermocouple junction with gold or silver metal and screening the couple with a silver shield. Charts are provided for applying correction to silver-shielded thermocouples. Heat transfer from the gas to the couple is improved by drawing part of the gas at high velocity over the couple as in the aspirated-type probe. Thermocouple wire of zero diameter would have no loss. Temps can be read on different gauge wires and extrapolated to zero dia. By passing part of the hot gas through two orifices and a cooling chamber its temp can be calculated from the lower temp, the pressure drops, and the orifice equations.

References are given for each type of measuring device. R. W. G.

2186. Distant indicating and recording rotameters. Anon. *Fluid Handling*, Apr. 1950 (5), 137–8.—Meters capable of indicating and recording the rate of flow of all fluids, including opaque and corrosive liquids, are specified. The flow controls the height of a metal bob in a tapered vertical tube. A small piece of iron attached to the bob affects the ratio of the outputs from two secondary coils of a transformer. The instruments are said to be largely independent of visc. D. H.

2187. Characteristics of ring balance mechanical flowmeters. C. W. Work. *Refiner* 1950, **29** (6), 89–90.—A ring-balance flowmeter has the following special characteristics which may warrant consideration for application to unusual conditions: (1) the range is easily adjustable; (2) no stuffing-boxes are required, and by using suitable

pressure parts flow in high-pressure lines can be measured; (3) two rings can be mounted in one case, and both made to record on the same chart; (4) by the use of suitable mechanism it is possible to apply corrections or other variables to the pen mechanism, *e.g.*, temp measurements may be applied to obtain heat flow.

R. W. G.

2188. Variable area flowmeters in the petroleum industry. Part I. Basic Design. R. W. Fritzsche. *Refiner*, 1950, **29** (3), 123–9.—The basic flow equation for orifice meters and rotameters is $V = AC[2gh]^{\frac{1}{2}}$. In the former the measurement is dependent on the variable head h, in the latter the flow is linearly related to the variable area A, C being a constant. For a rotameter type instrument the equation becomes,

$$Q = A_a C\left[\frac{2gV_f(\rho_f - \rho_L)}{A_f\rho_L}\right]$$

in volume units. Q being flow rate, A_a annular area, C a constant, V_f volume of float, A_f max cross-sectional area of float, ρ_f and ρ_L specific gravities of float and fluid respectively. Other equations are given for weight flow rate, liquid density, and gas-flow corrections. The familiar plumb-bob-shaped float is adversely affected by viscosity. Flats of the guided type have been developed which are almost immune to viscosity changes over a limited range. A drawing is given of the predictable float, and graphs are supplied for obtaining the flow coefficient for this type of float.

R. W. G.

2189. Temperature gradient in solvent extraction of lubricating oils. E. J. Reeves and E. P. Hardin. *Refiner*, 1950, **29** (1), 89–90.—The effect of a temp gradient between raffinate and extract outlets on efficiency of extraction was investigated experimentally as a result of the many patents concerning commercial practice. Data were obtained for furfural extraction of lubricating-oil distillates on a commercial unit and a three-stage laboratory extraction unit (the approx equivalent efficiency of commercial furfural units). The data showed the effect of temp gradient to be negligible. R. W. G.

2190. The graphic panel in automatic process control. L. Gess. *Refiner*, 1950, **29** (3), 110–14.—The development and advancement in pneumatic transmission over the last fifteen to twenty years has made graphic panels in their present form possible. Schematic diagrams illustrate the development of compact remote instrumentation. Two types of graphic panel are described. In the first, indicating instruments only are mounted on a compact flow diagram. Setting units are mounted below this, and room is available for recorders. In the second type setting units are mounted on a larger flow diagram in their correct relative positions. Less space is available for recorders. In both types the controlling units are mounted elsewhere. It is claimed that graphic panels assist in the training of operators. R. W. G.

2191. Pressure drop in gas and vapour line. P. Buthod. *Refiner*, 1950, **29** (4), 157–60.—With a constant friction factor, an ideal gas, and isothermal conditions a relationship is derived between the following groups:—$\frac{G^2T}{MP_1^2}$; $\frac{L}{D}$ and $\frac{P_2}{P_1}$ for gas flow. Assuming a friction factor of 0·004, a chart is presented for determining the value of these groups. If the friction factor is other than 0·004 a correction is applied to $\frac{L}{D}$. When compressibility does not vary greatly the correct pressure drop can be obtained by multiplying $\frac{P}{P_1}$ (from chart) by the compressibility factor. R. W. G.

PRODUCTS.

Chemistry and Physics.

2192. Socony-Vacuum discloses synthetic lubes from olefins. P. J. Gaylor. *Petrol. Process.*, 1950, **5** (5), 516–17.—A series of patents issued to Socony-Vacuum Oil Co., U.S.P. 2,500,159–2,500,167 inclusive, on the production of synthetic lubricants from

1-decane and similar hydrocarbons is briefly reviewed. Thermal polymerization of the hydrocarbon is common to most of the patents, the conditions being around 700° F temp and 200–1000 p.s.i. pressure in the presence of hydrogen or carbon monoxide or both, or small amounts of styrene or with lead tetra-acetate. Yields as high as 66% are claimed for an oil of 141 V.I., −10° F pour point, 16·6 Br No. and 0·84 sp. gr. from 1-decane. D. W. F.

2193. New approach to the synthesis of ethylenic compounds. E. A. Braude, J. A. Coles, and C. J. Timmons. *Nature*, 1950, **166**, 58.—The synthesis of unsaturated compounds, particularly those containing double bonds adjacent to a C atom carrying another functional constituent, can readily be accomplished through the α-alkenyl lithium derivatives. For example, pure *iso*butenyl bromide reacts readily with Li in dry ether, and after adding excess solid CO_2 the following compounds were found: 2 : 5-dimethyl hexa-2 : 4-diene (35%), β-β-dimethyl acrylic acid (7%), and phorone (15%). Alkenyl chlorides can also be used.

α-alkenyl lithium derivatives readily undergo the expected reactions with aldehydes, ketones, carboxylic acid derivatives, etc., and many of the compounds undergo molecular re-arrangement to give other unsaturated systems, of which some examples are described. H. C. E.

2194. The $CH_2{:}CH{\cdot}CH_2{-}CH_3$ bond dissociation energy and the heat of formation of the allyl radical. A. H. Sehon and M. Szwarc. *Proc. Roy. Soc.*, A, 7.7.50, **202** (1069), 263–76.—The results are given of an investigation into the pyrolysis of butene-1 in which a flow technique was employed and toluene was used as a carrier gas. The results showed that butene-1 was decomposed into allyl and methyl radicals according to the equation: $CH_2{:}CH{\cdot}CH_2{-}CH_3 \longrightarrow CH_2{:}CH{\cdot}Ch_2 + CH_3$. Methyl radicals were removed by reaction with toluene, giving methane and benzyl radicals. The rate of the initial decomposition was measured by the rate of formation of methane. The decomposition was found to be a homogeneous first-order gas reaction. The activation energy was calculated at 61·5 k.cal/mol and it was identified with the $CH_2{:}CH{\cdot}CH_2{-}CH_3$ bond dissociation energy. Taking $D(CH_2{:}CH{\cdot}CH_2{-}CH_3)$ at 61·5 k.cal/mol it was calculated from thermodynamical data $D/(CH_2{:}CH{\cdot}CH_2{-}H)$ at 76·5 k.cal/mol and the heat of formation of allyl radical at +30 k.cal/mol. The fate of allyl radicals is discussed, and the thermal stability of these is compared with that of benzyl radicals. W. H. C.

2195. The infra red spectra of trichlorethylene. ($CHCl = CCl_2$ and $CDCl = CCl_2$) and assymetrical tetrachlorethylene. ($CH_2Cl - CCl_3$ and $CD_2Cl - CCl_3$) from 2·5 μ to 25 μ. H. J. Bernstein. *Canad. J. Res.*, 1950, **28**, 132–9.—The infra-red spectrum of light and heavy trichlorethylene and assymetrical tetrachlorethane have been obtained between 2·5 μ and 25 μ. The modes of vibration of the two types of molecules are shown, and tentative assignments of the fundamentals have been made. N. T.

2196. Thermochemistry for the petrochemical industry. Part II. Paraffinic hydrocarbons. C_1–C_6. K. A. Kobe and E. G. Long. *Refiner*, 1949, **28** (2), 113–16.—Free energies of formation, heat of formation, heat of combustion, heat capacities, and enthalpies of paraffinic hydrocarbons C_1–C_6 are tabulated. R. W. G.

2197. Thermochemistry for the petrochemical industry. Part III. Mono-olefinic hydrocarbons. C_2–C_4. K. A. Kobe and E. G. Long. *Refiner*, 1949, **28** (3), 125–8.—Free energies of formation, heat of formation, heat of combustion, heat capacities, and enthalpies of ethylene, propylene, 1-butene, *iso*butene, *cis*-2-butene, and *trans*-2-butene are tabulated. R. W. G.

2198. Thermochemistry for the petrochemical industry. Part IV. Cyclo-paraffinic hydrocarbons. K. A. Kobe and E. G. Long. *Refiner*, 1949, **28** (5), 161–3.—Free energies of formation, heat of formation, heat of combustion, heat capacities, and enthalpies of *cyclo*pentane, methyl *cyclo*pentane, *cyclo*hexane, and methyl *cyclo*hexane are tabulated. R. W. G.

2199. Thermochemistry for the petrochemical industry. Part V. Aromatic hydrocarbons. K. A. Kobe and E. G. Long. *Refiner*, 1949, **28** (7), 145–8.—Free energies of formation, heat of formation, heat of combusion, heat capacities, and enthalpies of benzene, toluene, ethyl benzene, styrene, and cumene are tabulated. R. W. G.

2200. Thermochemistry for the petrochemical industry. Part VI. Acetylenes and diolefins. K. A. Kobe and E. G. Long. *Refiner*, 1949, **28** (10), 133–6.—Free energies of formation, heat of formation, heat of combustion, heat capacities, and enthalpies of acetylene, methyl acetylene, dimethyl acetylene, propadiene, butadiene 1-3, and isoprene are tabulated. R. W. G.

2201. Thermochemistry for the petrochemical industry. Part VII. Combustion gases. K. A. Kobe and E. G. Long. *Refiner*, 1949, **28** (11), 127–32.—Free energies of formation, heat of formation, heat of combustion, heat capacities, and enthalpies, % N_2, O_2 air, H_2, CO, CO_2 and H_2O are tabulated. R. W. G.

2202. Thermochemistry for the petrochemical industry. Part VIII. Sulphur compounds. K. A. Kobe and E. G. Long. *Refiner*, 1950, **29** (1), 126–30.—Heat capacities, free energy of formation, heats of formation and combustion, and enthalpies of S_2, SO_2, SO_3, H_2S, CS_2, and COS are tabulated. R. W. G.

2203. Thermochemistry for the petrochemical industry. Part IX. The halogens and halogen acids. K. A. Kobe and E. G. Long. *Refiner*, 1950, **29** (2), 124–8.—Heat capacities, free energies of formation, standard heats of formation, and enthalpies of F_2, Cl_2, Br_2, I_2, HF, HCl, HBr, and HI are tabulated. R. W. G.

2204. Thermochemistry for the petrochemical industry. Part X. The chloromethanes. K. A. Kobe and E. G. Long. *Refiner*, 1950, **29** (3), 157–60.—The heat capacities, free energies of formation, heats of formation, heats of combustion, and enthalpies of CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4, and $COCl_2$ are tabulated. R. W. G.

2205. Thermochemistry for the petrochemical industry. Part XI. Cyanogen compounds. K. A. Kobe and E. G. Long. *Refiner*, 1950, **29** (5), 89–92.—Free energies of formation, heats of formation, heats of combustion, heat capacities, and enthalpies of $(CN)_2$, HCN, CNCl, CNBr, CNI, CH_3CN, and $CH_2 = CHCN$ are tabulated. R. W. G.

2206. Detergency of carbon black in hydrocarbon solutions. Part II. Effect of dispersion medium on the particle size distribution of carbon black. F. H. Garner, C. W. Nutt, and M. F. Mohtadi. *J. Inst. Petrol.*, 1950, **36**, 292.—An electron micrograph study of the particle-size distribution of carbon black dispersed in toluene solutions of various additives has shown a correlation between the particle size and the dispersive power of the medium as measured by a standard setting-rate test. A. R. W. B.

2207. The kinetics of the interaction of atomic hydrogen with olefins, V. Results obtained for a further series of compounds. H. W. Melville and J. C. Robb. *Proc. Roy. Soc.*, A, 7.7.50, **202** (1069), 181–202.—An investigation has been made of the efficiency of the interaction of a hydrogen atom with a series of olefins, the olefins being members of the series obtained by progressively replacing the hydrogen atoms of ethylene by methyl radicals. The interesting generalization which emerges from the investigation is that the efficiency of interaction does not vary very much with the nature of the alkyl substituents in the molecule, and calculations involving the heats of addition of a hydrogen atom to a double bond confirm this generalization. The data presented are discussed critically in relation to information available on the reaction of CCl_3 radicals with olefins and of alkyl radicals with olefins, complete general agreement being demonstrated. W. H. C.

2208. Adhesion of solids and the effect of surface films. J. S. McFarlane and D. Tabor. *Proc. Roy. Soc.*, A, 7.7.50, **202** (1069), 224–43.—Previous work has shown that the friction between metals is due to the shearing of junctions formed by adhesion or

welding at the points of intimate contact. This suggests that when the load is removed the junctions should remain and an appreciable normal force should be needed to separate the surfaces. Experiments show that with clean, hard surfaces in dry air the adhesion is negligibly small. In moist air appreciable adhesion may be observed, and it is shown that this is due to the surface tension of a thin film of adsorbed water. The surface-tension forces due to thin films of liquid trapped between solid surfaces may be very large. Under certain conditions the viscosity of the liquid may also be important. The absence of adhesion between clean, hard surfaces is not due to the non-formation of metallic junctions. Experiments show that it is due to the released elastic stresses which break the junctions one by one as the load is removed. With very soft metals, such as lead or indium, where the effect of released elastic stresses is very much less important, marked adhesion is observed in air, if the surfaces are freed of grosser contaminants. This adhesion provides direct evidence for the formation of metallic junctions by a process of cold welding or pressure welding at the points of contact. If the surfaces are covered with oxide films of appreciable thickness, the amount of metallic interaction is diminished with a corresponding reduction in the adhesion. Lubricant films have a similar effect, and in general those materials which are most effective in reducing the adhesion are also most effective, as boundary lubricants, in reducing the friction. W. H. C.

2209. Studies on Foams. II. Foam formation and the volume contraction of liquid mixtures. M. Nakagaki. *Bull. Chem. Soc. Japan*, 1949, **22** (1), 21–4.—The foam formations of the ternary system methyl alcohol–ethyl alcohol–water have been determined, and the following binary systems have been studied : *n*-propyl alcohol–ethyl ether, methyl alcohol–ethyl ether, ethyl acetate–ethyl ether, *n*-propyl alcohol–methyl alcohol, *n*-propyl alcohol–ethyl acetate. The results of the ternary systems are recorded in triangle graphs showing : foaminess, surface tension, foam duration, viscosity, and volume contraction. Foaminess and foam duration have been tested by shaking the liquid for 30 sec in a test-tube and measuring the height of foam at the end of shaking, and the time required for collapse of foam zone. Viscosity was measured with Ostwald's viscometer, and the surface tension was measured with Traube's stalagmometer. Molar volume contraction was calc from the density data obtained with an Ostwald's pycnometer. It was found that the volume contraction is closely connected with the foaming properties. This is interpreted in relation to the micelle formation of mixtures. W. H. C.

2210. Flame length and its heat radiation. S. Yagi. *Bull. Chem. Soc. Japan*, 1949, **22** (3), 97–104.—This contribution includes work reported over ten years covering studies on : luminous flames, turbulent diffusion, flame length, flame radiation, and five other papers by the author. A diagram is given of the burner used. Measurement of flame length is described. The length of flame is made from photographs taken in front of a bright scale background. The relationship between (flame length, L cm)/(nozzle diameter d cm) and (fuel gas velocity at nozzle opening u cm/sec) $\times$ (d cm) is shown in the graph for several nozzle diameters. At the lower value of ud, L/d increases almost proportionally to ud, and at the higher ud, L/d is almost independent of ud, tending to L/d = 50–70. The two states of flame mentioned are seen in the photograph of flames. One is a diffusional flame or laminar-flow flame, the other, a turbulent flame. A transitional region between the two states can be seen in the photograph. A theoretical consideration of burning rate is made, and the effect of primary air is described. The method used for measuring the radiant heat of the flames, the data obtained when using town gas and town gas plus 6, 8, and 10% acetylene, and equations for computing the radiant heat are given. The relation of experimental burner to industrial burners is shown. The percentage of the amount of heat emitted per total heat content of fuel used, n, varies with ud and d as shown in the graph. The spectral radiation of luminous flames is described. Emission and absorption spectra data of luminous flames are shown. W. H. C.

2211. The molecular orbital theory of chemical valency. III. Properties of molecular orbitals. G. G. Hall and J. Lennard-Jones. *Proc. Roy. Soc.*, A, 7.7.50, **202** (1069), 155–65.—The discussion of molecular orbitals and equivalent orbitals, given in previous papers, is carried a stage further. It is shown that certain molecular pro-

perties can be evaluated using either equivalent or molecular orbitals. On the other hand, a study of the changes produced by ionization demonstrates that molecular orbitals have a special significance and that certain energy parameters associated with them are closely related to ionization potentials. For the purpose of this discussion a perturbation theory is developed to deal with the changes produced in molecular systems when disturbed from their normal states. W. H. C.

2212. The molecular orbital theory of chemical valency. IV. The significance of equivalent orbitals. J. Lennard-Jones and J. A. Pople. *Proc. Roy. Soc.*, A, 7.7.50, **202** (1069), 166–80.—The theory of the transformation from molecular orbitals to sets of equivalent orbitals is discussed for the general case when there is more than one occupied molecular orbital of given symmetry and more than one equivalent set. The general transformation is worked out for molecules whose component atoms possess inner shells and lone pairs of electrons. The theory is illustrated by reference to some simple molecules such as water and ammonia. Finally, it is shown how the expression for the total energy of a molecule can be divided up in such a way that the interactions between its localized parts are dealt with separately. The significance of lone pairs of electrons in determining the shape of molecules is pointed out. W. H. C.

2213. Physical constants useful in petroleum refining. Foster Wheeler Corp. *Refiner*, 1950, **29** (5), 116–17.—Boiling points, liquid and vapour densities, critical constants, heat of combustion, and O.N. of fifty-three paraffins, naphthenes, olefins, diolefins, acetylene, aromatics, misc solvents, and misc gases are tabulated. R. W. G.

2214. Problem of viscosity and the synthesis of new lubricants. M. G. Hugel. *Bull. Ass. franç. Tech. Pétrole*, 1950 (82), 29–39.—Mol concn., the reciprocal of mol. vol. (mol. wt. $\times$ d), is most suitable variable for comparing with visc. In a homologous series the visc/mol concn curve has the same slope for all members. This rule is, however, not applicable to substances exhibiting association and, in fact, departure from the rule is a convenient method of determining association. Several numerical examples for various series are given. V. B.

2215. Vapour pressure, surface tension, viscosity and equilibrium proportions of ideal mixtures (1). M. Roegiers. *Petroleum*, Oct. 1949, **12** (10), 256–8.—Considering the kinetic energy of molecules and intermolecular attraction energy, the Van der Waal's law of corresponding states, the Pitzer statement that the law of corresponding states applies to fluids, the molecules of which are free rotating, and the Boltzmann formula, connecting entropy to the thermodynamic probability of the macroscopic state, the following isothermal laws, confined to ideal mixtures, are derived :

1. Vapour pressure/blending proportions of the vapour phase.
2. Gaseous viscosity/blending proportions of the vapour phase.
3. Surface tension/blending proportions of the liquid phase.
4. Liquid viscosity/blending proportions of the liquid phase.
5. Vapour pressure/blending proportions of the liquid phase.
6. Equilibrium proportions of the liquid/vapour phases.

The paper is in three parts, part one dealing entirely with theoretical considerations. R. E. P.

2216. Vapour pressure, surface tension, viscosity and equilibrium proportions of ideal mixtures (2). M. Roegiers. *Petroleum*, Feb. 1950, **13** (2), 39–41.—Practical equations have been derived for each of the laws considered theoretically in part one. Experimental verification of the isothermic law " liquid viscosity/blending proportions of the liquid phase " of ideal mixtures has been made using various binary systems of refined Newtonian petroleum oil fractions with widely different viscosities. Calculated visc were usually found to be within 1% of the experimental data.

An example for the calculation of the equilibrium proportions of an ideal binary mixture is given. R. E. P.

2217. Vapour pressure, surface tension, viscosity and equilibrium proportions of ideal mixtures (3). M. Roegiers. *Petroleum*, Apr. 1950, **13** (4), 83–4.—Contains graphical illustrations and describes a mechanical acid, or abacus, devised to solve the laborious equations involved in a calculation of the viscosity of binary ideal mixtures. (See abstracts 2215 and 2216.)

The abacus can also be used for the calculation of the equilibrium proportions of the liquid/vapour phases of such mixtures.

An appendix gives nomenclature of symbols used in the three papers. R. E. P.

2218. Conditions of miscibility. A. H. Stuart. *Petroleum*, Apr. 1950, **13** (4), 85–6.—Conditions for complete miscibility are discussed briefly. It is shown that the failure of two liquids to mix is due to the presence of a positive surface tension at the interface. Miscibility can be improved by the addition of a third compound which reduces the interfacial forces to near zero. Such compounds are called blending agents, and are of great use in industry, *e.g.*, benzene is used in mixing methanol with petrol, anhydrous ethyl alcohol for mixing methanol and petrol to give a mixture of high water tolerance. R. E. P.

2219. Diffusional properties of multicomponent gases. C. R. Wilke. *Chem. Engng Prog.*, 1950, **46** (2), 95–104.—An expression for the effective diffusion coefficient of a gas with respect to a multicomponent mixture of stagnant gases, derived from the Stefan–Maxwell diffusion equations, is discussed and compared with exact solutions of the diffusion equations for various types of diffusion, and applications to the calc of visc of gas mixtures are outlined. Approx methods for the calc of rates of diffusion in complex mixtures for stagnant films and also with simultaneous diffusion of all components are presented; the effects of simultaneous diffusion on mass-transfer coefficients are also discussed. J. G. H.

2220. Significance of properties of petroleum products. XIII. Carbon residue. R. L. Martin and C. G. Stephens. *I.P. Review*, 1950, **4**, 226.—The tendency of gas oils, diesel oils, fuel oils, and lubricants to coke when heated has a considerable significance in assessing quality. This property, known as the carbon residue, is determined by one or both of two long-established methods, the Conradson test and the Ramsbottom test. Each assesses the coke-forming tendency of an oil when the oil is burned under controlled conditions in a limited supply of air. The results of such tests (which can be correlated) should always be considered in relation to other analysis results. The significance of the results upon fuel oils and lubricants, and troubles which result from high values are discussed in terms of the type of engine employed. R. H.

Analysis and Testing.

2221. Application of radioactive tracers to improvement of fuels, lubricants and engines. P. L. Pinotti, D. E. Hull, and E. J. McLaughlin. *S.A.E. Trans.*, Oct. 1949, **3** (4), 634–5.—The use of radioactive piston-rings in research on engine wear is described. This method enables accurate and reproducible wear data to be obtained by measuring the amount of radioactive iron in the oil after only 2–4 hr testing. Other advantages include a marked reduction in the size of fuel and oil samples and the elimination of engine disassembly between tests. Precautions necessary for handling the activated parts and oil are summarized, and conditions necessary to ensure reproducibility of results are enumerated. Other applications of the radioactive technique to engine testing are indicated. J. G. H.

2222. Nuclear fission used to improve oil processes. Anon. *Refiner*, 1950, **29** (1), 131.—A brief reference to three uses of radioactive tracers in the oil industry :—

(1) Radioactive carbon to follow gasoline molecules through the process of refining.

(2) Radioactive piston-rings used in engine lubrication tests to show wear—leads to tests of shorter duration.

(3) Identification of different crudes or products following one another in a pipeline by adding one billionth of an ounce of radioactive barium to the shipment.

R. W. G.

2223. Simple variable space infra-red absorption cell. J. V. White. *Rev. sci. Instrum.*, 1950, **21**, 629.—A variable-space liquid-absorption cell is described for use in the infra-red spectral region. Its range of thicknesses from 5 mm to less than 10 μ makes it suitable for the compensation of absorption by solvents in a double-beam spectrophotometer; its accuracy and reproducibility are sufficient for most direct qualitative and quantitative measurements. The min volume is approx 1 c.c., and leakage is negligible. Its windows of rock salt may easily be removed and repolished. (Author's abstract.) H. C. E.

2224. Non-destructive weld testing. Anon. *Fluid Handling*, Mar. 1950 (4), 87–90.—Testing of welds in the field by a portable ultrasonic apparatus is detailed. Oscillations from a piezoelectric crystal are transmitted through an oil film to the welded joint, and travel through the metal in a conical beam whose semi-angle θ is $= \sin^{-1} K\lambda/d$, where λ = wavelength, d = diameter of source, and K = constant. This beam is reflected from surfaces, or flaws and inclusions, and picked up by another crystal which feeds it to a cathode-ray oscillograph. Waves reflected from a flaw arrive before those from the other surface, and by their characters and intensity, the seriousness and nature of the fault can be estimated. D. H.

2225. Olefins in naphthas. G. U. Dinneen, J. R. Smith, and J. S. Ball. *Refiner*, 1950, **29** (5), 129–34.—Three different methods of estimating olefin content were carried out on ten shale-oil naphthas and nine petroleum naphthas. The nitrogen tetroxide and silica-gel methods gave comparable results which agreed with olefin contents found by difference, while the bromine-number method gave results 3–35% units high. It is indicated that substitution reactions and the presence of sulphur and nitrogen compounds lead to high results for the bromine-number tests. This last method is further criticized owing to the uncertainty of the average mol. wt. of the olefins in the sample. The use of bromine numbers for estimating olefins is not recommended for shale-oil naphthas, and should be used with caution with cracked-petroleum naphthas unless the olefin content is low or its characteristics known.

A good bibliography is included. R. W. G.

2226. Determination of small amounts of sulphur in organic compounds. H. N. Wilson and H. T. Straw. *J. Soc. chem. Ind.*, Mar. 1950, **69** (3), 79–82.—A vertical quartz-tube method in which air is drawn through tube packed with V_2O_5 catalyst supported on alumina. Tube can be electrically heated up to 1000° C and solution fed in from burette via a capillary. Vapours absorbed in H_2O_2 and determined volumetrically as H_2SO_4 or gravimetrically as $BaSO_4$. Claims of wide application from petrols to creosote oils, speed of determination, and reproducibility of at least $\pm 5\%$ with S contents of 0·001–0·100%. H. J. B.

2227. Unsaturation in petroleum as indicated by halogen addition methods. A. Winward and F. H. Garner. *J. Soc. chem. Ind.*, May 1950, **69** (5), 147–53.—Investigation mainly confined to interpretation of iodine values (Hanus) on straight-run gas oils. Variation of iodine value with reagent concentrations and reaction times first investigated. High iodine-value fractions concentrated and shown by HBr evolved to be iodine *substitution* and not *saturation*. Some evidence to show this may be due to the presence of 1 : 3 : 5-trialkyl-substituted aromatics of the mesitylene and *iso*durene type. H. J. B.

2228. Selective adsorption of hydrocarbons. II. G. Spengler and K. Krenkler. *Erdöl u. Kohle*, 1950, **3**, 317–21. (Cf. Abstract No. 1280/50.)—Adsorption analyses of known mixtures were carried out using a column of either silica gel or activated charcoal. Curves were obtained relating ml of filtrate to n. Preliminary tests with binary mixtures benzene/n-hexane and *cyclo*hexene/n-hexane showed that small concn differences could be detected and that quant determination of aromatics and olefins

can be made. Adsorption affinity for branch-chain olefins decreases with increasing chain length in case of silica gel and increases for charcoal. In analysis of gasolines shape of *n*/ml-filtrate curve can give qual indication of nature of preponderant hydrocarbon group; thus curves initially rising when using charcoal and falling with silica gel indicate *n*-paraffins, falling on both adsorbents, *iso*paraffins, and rising on silica gel and falling on charcoal, naphthenes. Solvent used was *n*-hexane with a gasoline/solvent ratio of 1/3. Curves are given for numerous gasoline samples, and it is shown that, in some cases, conventional analyses are erroneous. Good separation was also obtained for α-methylnaphthalene/cetane mixtures. V. B.

2229. Determination of organic functional groups by chemical means. S. Siggia. *Anal. Chem.*, 1950, **22**, 378–81.—In order to use a chemical reaction for determining a functional group, at least one of the reactants or products must be measurable. Reactions that liberate or consume an acid, base, oxidant, reductant, or gas are particularly adaptable for quantitative purposes. Several reactions which liberate or consume easily determinable compounds such as water can be used to measure functional groups. Reactions that yield precipitates also have analytical possibilities. Equilibrium, incomplete reaction, poor end points, and interferences are the troubles usually encountered. Techniques are available for minimizing these difficulties. J. S.

2230. Infrared analysis of phenol, cresols, xylenols and ethyl phenols. R. A. Friedel, L. Pierce, and J. J. McGovern. *Anal. Chem.*, 1950, **22**, 418–20.—Qualitative and quantitative analyses by means of infra-red spectrometry have been carried out on carbon disulphide polutions of phenol and C_7 and C_8 alkyl phenol mixtures separated from coal-hydrogenation oil. The base-line method of calculation permitted accurate quantitative results to be obtained from the original curves used for qualitative interpretations. Measurements on six bands used in analysis disclosed that deviations from Beer's Law linearity was practically zero. Data are presented showing the results obtained on synthetic blends as well as on actual samples. J. S.

2231. Determination of certain ortho-substituted phenols. H. H. Willard and A. L. Wooten. *Anal. Chem.*, 1950, **22**, 423–4.—A colorimetric method for the determination of *o*-phenyl-phenol, or *o-tert*-butyl-phenol in the presence of their para-isomers is based on the formation of their aristols (thymol iodides) and subsequent extraction with toluene. The optimum amount of *o*-phenyl-phenol is about 2·5 mg and of *o-tert*-butyl phenol is about 0·5 m.g. An accuracy of about 1% is practical. J. S.

2232. Evaluation of vacuum flash vaporization curves from atmospheric true boiling point distillation. R. K. Okamoto and M. Van Winkle. *Refiner*, 1950, **29** (1), 91–6.—A method and graphs are presented for obtaining 50% flash temp and flash curve slope at sub-atmospheric pressures from the atmospheric T.B.P. curve based on volume percentages. The method is not recommended for stocks showing abnormal distillation-curve characteristics, such as bright-stock naphtha solution. R. W. G.

2233. Exothermic decomposition of nitromethane. W. G. Cass. *Airc. Engng*, Aug. 1950, **22** (258), 238.—Pre-war Italian experiments on nitromethane (Ergol) as a prospective fuel for stratospheric engines are described. Shock and detonator tests were made with loads up to 2 kg and fall of 1·95 m, and the nitromethane remained stable at these maximum limits. Initial qualitative experiments were made to determine exothermic decomposition. It was found that there was substantial decomposition at 400° C, and from 50 cc were obtained 9 litres of gaseous combustible mixture and 15 cc of condensate consisting in great part of liquid undecomposed nitromethane. First high-pressure work was begun as early as 1933, using a stainless-steel bomb into which nitromethane was injected under pressure. Results of tests using both continuous and intermittent injection are shown and apparatus illustrated. Although laboratory tests appeared to give hopeful results, they were not confirmed by actual full-scale test, at least not when a power pump run from a motor was used for injection at 1800 r.p.m. instead of slow hand operation. An explosion occurred which blew pump to pieces and seriously injured engineer in charge. It was therefore decided for time being to renounce use of nitromethane for this purpose. U. N.

2234. Investigation of sulphur in motor fuels—effects on engine operation. R. E. Jeffrey, J. B. Duckworth, and E. J. Gay. *Refiner*, 1950, **29** (5), 111–15.—(*Presented to motor fuels session, mid-year meeting. A.P.I. divn of refining, Cleveland.*)—Presented are the results of a 4½-year programme supported by A.P.I. and Soc. Auto Engrs, sponsored by C.R.C. Inc., and assisted by a large number of companies.

From the results of laboratory dynamometer tests a field-test programme was arranged comparing high sulphur fuels (0·25–0·30% S) with low sulphur fuels (less than 0·10% S). Sixty-two vehicles in seven fleets, ranging from passenger cars to heavy trucks, with varying duties, and in representative varying iccations were co-opted. Manufacturers provided new or rebuilt engines and new mufflers. To save transportation problems and expense disulphide oil was added to the normal fuel.

On heavy duty service essentially no difference in wear was reported.

On light or medium duty services with intermittent stops, such as door-to-door deliveries, more wear was reported for the higher-sulphur fuels.

The use of heavy duty crankcase oil lowered cylinder wear with low-sulphur fuels, but did not appreciably affect the wear with high-sulphur fuels.

Muffles and exhaust systems were not adversely affected by high-sulphur fuels. Tables are presented showing wear in cylinders and rings. R. W. G.

2235. Determination of the water content of motor fuels. S. J. W. Pleeth. *J. Inst. Petrol.*, 1950, **36**, 345.—The literature has been examined for methods of determining water contents suitable for use with motor fuels containing water-soluble constituents. Three methods have been compared in the laboratory : Dietrich (using magnesium nitride), Schutz (using calcium carbide), and Fischer (using iodine and sulphur dioxide in pyridine). Of these the Fischer gave the most consistently accurate results, and is to be preferred. A. R. W. B.

2236. Load capacity rating of lubricants. V. H. Brix. *J. Inst. Petrol.*, 1950, **36**, 295.—It has always been difficult to rate lubricants in terms of their ability to lubricate, this property being usually expressed in terms of the load capacity, film strength, etc., as determined on some arbitrary test machine. Some success has been achieved in recent years with the development of the I.A.E. (now the M.I.R.A.) 3¼ in oil-testing machine. This method possesses, nevertheless, certain drawbacks which limit its use. A machine is described which employs simple test-pieces which can be re-used indefinitely, and which is easy and rapid in operation. The results have a similar trend to those obtained on the I.A.E.-type gear machine, and have shown useful correlation with service conditions. A. R. W. B.

2237. Microdetermination of knock characteristics of motor fuels. J. Alenander, Jr. and C. Pfeiffer. *Anal. Chem.*, 1950, **22**, 476–80.—A method is described whereby motor and research O.N.s can be determined on 20-ml samples of fuel with an accuracy approaching that of the standard knock-engine-test procedures. This method employs the customary knock engine, and involves two alterations in design and one change in procedure. The amount of fuel in the fuel-inlet system is reduced from 60 to 1 ml by the use of a specially designed glass-capillary inlet system. The running time necessary for the standard knock meter to reach equilibrium is eliminated with negligible loss in accuracy by its replacement with an instantaneous-recording knock meter. The running time necessary for the adjustment of the C.R. and the fuel–air ratio is reduced by the use of several manipulative short cuts, including a continuously variable fuel–air ratio on different fuels, was 1·42 and for thirty-eight motor octane determinations was 1·15. J. S.

2238. The magneto-optical rotation of pure hydrocarbons and its application to the analysis of mixtures. J. B. Westerdijk, H. I. Waterman, H. F. O. Span, H. Boox, and K. van Nes. *J. Inst. Petrol.*, 1950, **36**, 281.—The results of measurements of the Faraday-effect of pure hydrocarbons by Foehr and the authors are discussed. Different structural groups of a molecule contribute additively to a constant D, which is a function of the measured Verdet-constant and other physical properties of the substance. This additivity does not hold for the contributions of ramifications, which are irregular. This means that the constant D cannot be safely used in structural group analysis if the number of side-chains of the average molecule in a mixture of

hydrocarbons is to be determined. In this case, however, the Verdet-constant itself may give useful information about the number of ramifications, and this is shown for alkanes with side-chains. It is shown that the constant D is a linear function of the square of the frequency of the light source if this frequency is sufficiently far removed from the range where absorption occurs.

The authors are convinced that measurements of the magneto-optical rotation may in future be regarded as belonging to the useful methods of determining the structure of the average molecule in hydrocarbon mixtures, especially in the range of low molecular weight. A. R. W. B.

2239. Interim report of the oxidation panel of standardization sub-committee no 6. Anon. *J. Inst. Petrol.*, 1950, **36**, 336–44.—The object of the work undertaken is to standardize an oxidation/corrosion test capable of distinguishing between straight mineral oils and H.D. engine oils approved to U.S. Navy Spec. 14–0–13 or U.S. Army Spec. 2–104B. As an interim measure differentiation is being considered on the basis of corrosion only, and on this basis, using a test piece of pure lead as a stirrer, the modified Sunbury beaker corrosion test gives the required differentiation. The basis of measurement is the cumulative loss in weight of the test pieces over two successive 6-hr periods at a temp of 140° C, catalysts and test-pieces being changed at 2-hr intervals. Although reproducibility is not good, a clear distinction is obtained between the two types of oil.

Work is also being pursued with the modified Indiana oxidation/corrosion test, but development of this method has not proceeded as far as with the Sunbury test.
A. R. W. B.

2240. Process research engineering—its scope, purpose and procedure. J. H. Hirsch. *Petrol. Process.*, 1950, **5** (5), 502–4.—Presented before the Annual Meeting of the Amer. Soc. Chem. Engrs, Pittsburgh, Dec. 4–7, 1949, this paper gives an account of how Gulf Research and Development Co. tackle process research problems. Process research engineering comprises the mathematical and engineering treatment of process research, including the correlation of engineering and pilot-plant data and the economic evaluation of the process. Certain research staff assignments are mentioned.
D. W. F.

2241. Determination of bloom of lubricating oils. A. Kinsel and J. Phillips. *Refiner*, 1950, **29** (5), 93–6.—By its " cast " or " bloom " it is generally considered possible to tell whether a lubricating oil has a paraffin or naphthene base. A simple apparatus and method for determining and expressing the bloom quantitatively are described. The bloom is matched against Lovibond colour glasses, the blue, yellow, and red series being required. The results are expressed as x blue or x yellow, x being the excess number of the blue glasses over the yellow glasses or vice versa. As it is much more difficult to measure intensity and it serves no useful purpose, there is no need to report the number of red glasses used.

The basis of this method of reporting the results is due to the fact that Lovibond colour glasses are externally equivalent and additive, *i.e.*, 1B + 1Y = 1G, and 1B + 1Y + 1R = 1 black. R. W. G.

2242. Fisher electroviscometer range extended to 50,000 centipoises. Anon. *Laboratory*, 1950, **19** (5), 122.—The range of the Fisher electroviscometer (see Abstract No. 580) has been extended to 50,000 cp by the introduction of a new accessory bobbin. The vise of a number of asphaltic and tar products can be measured at some of the standard temps, and also those of semi-fluid greases, automatic transmission fluids, paints, pigments, synthetic varnishes, etc. C. N. T.

2243. Recording mass spectrometers. R. M. Ilfeld. *Oil Gas J.*, 6.7.50, **49** (9), 50.—The mass spectrometer can be used for both qualitative and quantitative measurements, and normal sensitivity of the instrument is 1 part in 10,000, which can be adjusted under special conditions to 1 part in 100,000.

The mass spectrometer analyses a gaseous mixture first by ionizing the gas and then by sorting these ions according to their mass.

The new General Electric instrument is described, and the operating principle is illustrated schematically.

Its use assists in setting up distillation columns for optimum operation, and analysis of process streams in thermal cracking units permits evaluation of potential output and efficiency. G. A. C.

2244. Application of polarography in the petroleum industry. P. W. West and C. H. Hale. *Refiner*, 1950, **29** (6), 109–11.—The sensitivity of the polarograph permits the analysis of solutions which are one-millionth molar with respect to the substance to be determined. Speed in carrying out these determinations as compared to chemical methods is an important advantage. Techniques have been developed which make the polarograph more and more useful in refinery analyses. These techniques usually consist of slight chemical preparation. Examples of refinery analyses which can be carried out on a polarograph are: tetra-ethyl lead in gasoline; Zn, Cd, Cu, Sn, Sb, Cr, and Na in lubricants; elemental sulphur; H_2S in hydrocarbon gases; major components and trace impurities in catalysts, *e.g.*, Ni in presence of Co; oxygen content of cooling waters, etc.; naphthalene, acenaphthene, and β-methylnaphthene in kerosine and light gasoline; aldehydes in alcohols, olefins, etc.; substituted acetylenes and olefines.

References are given for details of most of these determinations. R. W. G.

2245. Resin and drying oil tests. C. C. Hartman, C. F. Pickett, and F. Scofield. *Paint Mnfr.*, Aug. 1950, **20** (8), 280.—The tests are not described in detail, but their purposes and the information which they may be expected to furnish are discussed. Tests mentioned for drying oils include heat-bodying, acetone number, measurement of completeness of esterification, conjugation, and iodine number. A method of measuring " set-to-touch time " on oils containing drier has recently been developed.

Because of the many and varied uses of shellac and other lac resins certain well-established tests are used to determine purity. In addition, certain other tests are employed to ascertain thermoplasticity, bleachability, etc. Detection and estimation of resin is probably one of the most important items of shellac analysis.

Work on synthetic resins covered the determination of the usual constants of resins, development of tests for identity and purity, and tests related to expected use of resins.

Precipitation of non-volatile matter by addition of a non-solvent for the resin (usually alcohol) gave interesting results, and may be suitable for determination of non-volatile content of many resins.

With increasing complexity of materials available to the coatings industry there is less emphasis on the adoption of standard specifications for materials and more on development of methods by which the user can write a specification to meet requirements of his particular problem. D. K.

2246. Photography proves valuable tool at Sinclair's East Chicago refinery. R. D. Herlocker. *Oil Gas J.*, 6.7.50, **49** (9), 40.—Sinclair Refining Co. have demonstrated that photography can give valuable assistance in new construction and engineering work, from breaking ground to completion.

Photographs provide a permanent and convenient record of equipment failures and permit quick return of repaired unit to service.

Photomicrography is also used for control of operations on the stills making paraffin distillates, to determine crystal structure of wax present.

A further use of photography is in recording results of bearing tests on heavy duty lube oils and greases. G. A. C.

2247. Gloss measurement. V. G. W. Harrison. *Paint Mnfr*, Aug. 1950, **20** (8), 277.—The four most important factors influencing a paint film are colour, gloss, surface smoothness, and texture. Gloss is due largely to light reflected from the surface. Usually this light is uncoloured, and under given conditions of illumination is concentrated near the angle of specular reflection. Methods of measurement of gloss are discussed. The work described has been carried out with matt to moderately glossy near-white papers, but results may be applicable to paints of high gloss or deep colour. Gloss is affected to a marked extent by surface irregularities. There are six literature references. D. K.

Crude Oil.

2248. Refinery processing of Lacq petroleum. J. Jochem. *Rev. Inst. franç. Pétrole*, 1950, **5**, 227–35.—Mixed base crude from Lacq (S.W. France) has following principal characteristics: d_{15} 0·928, S 3·9%, pour $< -25°$ C, characterization factor 12 +, E_{20} 36·5°, neut. val. 0·46, dist at 250° C 24%. It is processed at the Pauillac refinery of Shell-Berre in a two-stage (atm/vac) unit, of which flow diagram and operating conditions are given. Yields (% wt) are: gasoline (190/195° C E.P., O.N. 58, +0·03% T.E.L. 69) 9·8, kerosine 3·2, gas oil 17·5, light dist (E_{20} 2·4°) 15·5, heavy dist (E_{20} 3·6°) 2·1, bitumen (sp. gr. 25°/25 C 1·045, pen 87, S 6·6%) 50·6. Gasoline is refined by caustic washing and also requires stabilization for v.p. Crude and products contain H_2S, so NH_3 injection is used, both on dist unit and in storage tanks. Gas oil is good diesel fuel except for high (1·15%) S content. Vac distillates are waxy, and as they would yield only medium-grade lub. oil their use as cracking stock is recommended. V. B.

Gas.

2249. Alcoa's new plant uses natural-gas power source. L. C. McCaslin. *Oil Gas J.*, 3.8.50, **49** (13), 58.—The use of natural gas for 120 engine generator units for production of electrical energy at the Point Comfort Works of the Aluminium Co. of America is described.

Total output of the internal-combustion-engine plants will be 192,000 h.p. by eleven-cyl radial-type engines. Some 4000 ft of 4-in aluminium pipe has been laid for an experimental gas-gathering line, and 21½ miles of 4-, 6-, and 8-in pipe have been laid in Lavaca and Natagorda bays.

Natural gas is delivered at a pressure of 400–500 p.s.i.g., reduced to 60 p.s.i. Each engine consumes 13,000 cu. ft/hr under load, and about 30,000,000 cu. ft. gas/day will be consumed. Forty generators, driven by the above engines, will each produce 1000 kW (D.C.) and 125 kVA (A.C.). G. A. C.

2250. Use of liquefied gases for (propulsion of) motor vehicles (cars). S. Psarski. *Nafta*, June 1949, **5**, 143–5.—Use of liquefied gases would save petroleum, and it is more economical than use of compressed gas. Thermos bottles could keep losses down to 0·2%/hr high-pressure containers are heavy and dangerous, radius of travel of a 5-ton lorry between refills would be approx 200 km, as compared with 60–80 km with H.P. gas. Energy required to liquefy natural gas is only 50% higher than that required to compress it to 250 atm, although capital cost is higher. Thus liquefied gas should be used. M. S.

Engine Fuels.

2251. National motor-gasoline survey, winter 1949–50. O. C. Blades. *U.S. Bur. Mines Rep. of Invest.*, 4702, June 1950.—Test data are recorded of the properties of premium and regular motor gasolines produced in seventeen districts in the U.S.A. during the winter of 1949–50. Similar data for previous winters 1935–36 to 1948–49, and also for the summers 1936 to 1949 are given. Average octane ratings during the winter of 1949–50 were the highest observed in the surveys indicated and probably the highest in the petroleum industry to date. They were one and a half to two and a half units greater than those of the previous winter. Similar comparisons of other tests indicate a slight trend during the last four winters towards more volatile gasolines. W. H. C.

2252. Boiler fuels in marine diesel engines. III. Anon. *Motor Ship*, Aug. 1950, **31** (367), 182.—Report of discussion following paper by J. Lamb, read at Inst. of Marine Engrs, on "Further developments in the burning of boiler fuels in marine diesel engines." Speakers gave examples of the use of boiler and heavy fuels in practice, and discussed some of the problems arising from their use. U. N.

2253. Combustion in moving air. F. R. Caldwell, F. W. Ruegg, and L. O. Olsen. *S.A.E. Trans.*, Apr. 1949, **3** (2), 327–40.—A general review is presented of combustion problems arising from jet-engine developments at the National Bureau of Standards and elsewhere. Basic terms and concepts are discussed, factors affecting combustion are enumerated, and problems outlined include flame stabilization and combustion at low- and high-temp ratios. J. G. H.

2254. Gas turbine combustion efficiency calculations. J. G. Withers. *Aircr. Engng*, Aug. 1950, **22** (258), 218.—Data are presented which provide a rational basis for calculation of combustion efficiency. Principles involved examined critically, definitions clarified, and simple standard method of calculation, applicable to full range of operating conditions and fuels, developed. Alternative definitions based on ratio of actual to theoretical heat releases and of theoretical to actual fuel requirements discussed in relation to practical need for reckoning enthalpies above a datum temp. Enthalpies of reactants and products of combustion calculated with sufficient accuracy from empirical expressions, and appropriate heat of combustion of fuel defined and effect of temperature examined. Differences between generalized fuel- and enthalpy-ratio efficiencies determined under extreme conditions, and a practical formula developed. Finally, examination made of errors involved in measurements required for both heat-balance and exhaust-gas analysis methods of combustion-efficiency determination. Illustrated by tables and curves, and three literature references given. U. N.

2255. Diesel combustion temperatures—influence of fuels of selected composition. O. A. Uyehara and P. S. Myers. *S.A.E. Trans.*, Jan. 1949, **3** (1), 178–99.—Flame-temp data obtained with the electro-optical pyrometer developed by the University of Wisconsin are presented for a series of diesel fuels of selected composition, together with reproducibility data for the test engine and equipment. J. G. H.

2256. Combustion of diesel fuel. M. A. Elliott. *S.A.E. Trans.*, July 1949, **3** (3), 490–515.—The development of the diesel engine resulting in the imposition of more stringent operating conditions has rendered necessary a more detailed study of combustion with increased emphasis on chemical aspects. Previous studies of the theory of combustion have considered the process as occurring in four stages: the delay period, the time elapsing between injection and ignition; the period of rapid combustion; the stage of combustion during which the rate of combustion is controlled by the rate of fuel injection; and the period of after-burning. It is suggested that the combustion of diesel fuel is accomplished in two stages; the ignition-delay stage; and the inflammation stage. The ignition-delay stage comprises a period of physical delay and a period of chemical delay; the phenomena occurring during these periods are described in detail, together with the chemical processes encountered during the period of inflammation. Other points discussed include the significance of cetane number and of the products of incomplete combustion. J. G. H.

2257. Combustion characteristics of diesel fuels. E. W. Landen. *S.A.E. Trans.*, Jan. 1949, **3** (1), 200–6.—The examination of the end products of combustion of diesel fuel can be used to indicate conditions found in the combustion chamber. Data are presented from investigations in which the exhaust products from the precombustion-chamber type of engine were passed through a condensing system which cooled the products down to 0° F. Products were collected as a function of fuel: air rates for a given fuel, keeping b.m.e.p. constant with varying fuel composition. The amount of liquid and solid exhausted was found to depend on the engine and operating conditions; at low loads carbon exhausted is slight and increases as the smoke point is reached and the liquids exhausted decrease as the load is increased. Smoke as read on a smoke-meter follows the exhausted material; sulphur trioxide exhausted increases with increasing sulphur in the fuel, and also increases as the engine load is decreased. J. G. H.

2258. Composition and properties of diesel fuels—preliminary data. H. M. Smith. *S.A.E. Trans.*, Jan. 1949, **3**, 163–77.—The composition of two diesel fuels, one a

straight-run fuel and the other cat cracked, is discussed. Silica-gel and distillation techniques used are described, and physical properties of the fractions so obtained are enumerated. J. G. H.

2259. Effect of sulphur on T.E.L. requirements less by road than by " lab " ratings. Anon. *Petrol. Process.*, 1950, **5** (5), 492–4.—Condensed from a paper titled " Road effectiveness of tetra-ethyl lead as influenced by added sulphur," presented at the 15th Mid-Year Meeting of the A.P.I. Division of Refining, Cleveland, May 4, 1950, based on a report by D. H. Pulleyblank and W. G. Lovell. Eleven current commercial fuels have been tested for the effect of added sulphur (0·01–0·12%) on loss of O.N. as found by the normal lab knock tests and the Union-town road-rating method. The effect on the latter is found to be only 50% of that indicated by the former methods. The sulphur effect is evaluated as a T.E.L. efficiency, *i.e.*, the ratio of T.E.L. vol required by the low-sulphur fuel to that required by the fuel with added sulphur for the same O.N. The discrepancies are thought to be due to fuel-component separation and maldistribution in the multi-cylinder engine. D. W. F.

2260. The effects of sulphur in motor gasoline or engine performance. R. E. Jeffrey, J. B. Duckworth, and E. J. Gay. *Petrol Process.*, 1950, **5** (5), 494–7.—Taken from a paper of the same title presented by the authors at the 15th Mid-Year Meeting of the A.P.I. Division of Refining, Cleveland, May 4, 1950. Seven fleets of sixty-two vehicles dispersed over wide sections of the U.S. have been used for field tests for studying the effects on engine wear of motor gasoline with sulphur content of 0·25–0·30%, as compared with fuels of 0·056–0·14% sulphur content. A disulphide oil was used to raise the sulphur content of a normal gasoline to the higher level for the tests. The resulting data show the influence of the high-sulphur fuels may vary widely from a pronounced effect on cylinder and ring wear under certain operating conditions to no effect under continuous normal operation. This increased wear, however, is not consistent with general field-service experience. Valves, muffler life, and exhaust-system corrosion were not adversely affected. D. W. F.

2261. " Vitamin " capsules assure cold weather starting for automobile operations. Anon. *Refiner*, 1950, **29** (5), 118.—The development of an ethyl-ether-based starting fluid has been announced by the California Oil Co. The fluid is contained in $1\frac{1}{4} \times \frac{7}{8}$-in-dia gelatine capsules. For easy starting in cold weather (down to −25° F) the operator places a capsule in an adaptor on the dashboard and depresses the plunger. The capsule is punctured, and the fluid is injected through atomizing nozzles into the intake manifold. Due to its wide explosibility range and low ignition temp, the fluid–air mixture ignites easily and warms the combustion chamber for the normal fuel. Adaptors will cost $15 approx, and each start about $0·09. R. W. G.

2262. Antidetonant injection. C. H. Van Hartesveldt. *S.A.E. Trans.*, Apr. 1949, **3** (2), 277–87.—The possibilities of marked fuel economies with high C.R. engines are remarked, and it is noted that these cannot be made generally available until additional anti-knock quality is provided in the fuel used. The method of anti-detonant injection is suggested as a means to this end, and details are presented of the Vitameter unit evolved for this purpose. The requirements of anti-detonant fluids are outlined, and the possibilities of alcohol–water–T.E.L. anti-detonant injection are discussed in detail. J. G. H.

2263. Determination of the thermal structure of a combustion wave by fine thermocouples. R. Klein, M. Mentser, G. Von Elbe, and B. Lewis. *J. Phys. & Colloid Chem.*, 1950, **54** (6), 877–84.—By mounting a fine thermocouple in a strand of smokeless powder a determination is made of the variation of temp with time as the combustion wave passes over the thermocouple. Measurements of burning velocity then allow the determination of the temp distribution in the combustion wave. The effects of pressure and temp on the temp distribution in the wave are measured, and an analysis of a typical curve indicates qualitatively the distribution of the chemical reaction rate throughout the wave. D. F. J.

2264. New approach to evaluation of fuel volatility and associated engine variables. J. E. Taylor and H. J. Gibson. *S.A.E. Trans.*, Apr. 1949, **3** (2), 306–18.—The desirability of the production of motor fuels less volatile than those at present in general use is remarked, and the necessity for a procedure permitting the evaluation of the fuel-volatility engine relationship on a sound technical basis is stressed. Such a procedure is described, consisting of running the car at 20 m.p.h. road load and measuring its performance at the end of each minute of operation until it is fully warmed up. The measure of car performance is based on the speed attained at the end of 6 sec of full-throttle operation starting at 20 m.p.h. The procedure has proved fully reproducible and sufficiently sensitive to study the effects of variations in fuel or engine characteristics in warm-up performance. Points discussed in detail include test fuels, car characteristics, engine and operating variables, and customer reactions. The effect of distillation curve on warm-up performance is considered, and indicates that 50% point is of greatest importance as an index of volatility. J. G. H.

2265. Symposium on kinetics of propellants. Introductory remarks. R. E. Gibson. *J. Phys. & Colloid Chem.*, 1950, **54** (6), 847–53.—The introduction to the symposium on Kinetics of Propellants held under the auspices of the Division of Phys. and Inorg. Chem. at the 112th Meeting of the Amer. Chem. Soc., New York C., Sept. 15, 1947. An outline is given of the significance of the study of the kinetics of propellants, and the elementary ideas underlying the subject are presented. It is considered that although the discussions of the symposium are limited to a restricted field, the physical–chemical results will be of wider application. The papers presented at the symposium follow this article (pp. 854–954). D. F. J.

2266. Farm mechanization in relation to fuels. W. H. Cashmore. *J. Inst. Fuel*, 1950, **23** (132), 175.—Tractor-utilization surveys indicate that for many farm operations the tractor is working well below capacity. On comparison of these figures with tractor performances under varying loads it is seen that underloading appreciably lowers fuel efficiency. Proper use of the gears by the operator to give optimum loading aids fuel economy, as also do adjustments on the tractor to suit working conditions. Varying the weight on the back axle, jet and carburettor adjustment, and radiator temperature can increase overall fuel efficiency over a range of working conditions. Long-term improvements are to be expected from research and development into farm techniques and the design of implements and equipment. D. K.

2267. Exceptional performance of a nuclear otto-cycle engine using *n*-pentane as fuel. R. O. King, E. J. Durand, and A. B. Allen. *Nature*, 1950, **166**, 70.—A C.F.R. engine running at 400 r.p.m. was operated so that carbon black was formed within the cyl by the impingement of flame on the relatively cool surfaces in the combustion space. Under these conditions it was possible to operate at a mixture only 40% of the " correct " value, and the indicated thermal efficiency was then 53% at a usable compression ratio of 11·5 : 1. The usable C.R. 7·2 : 1 and thermal efficiency 32·5% were obtained at " correct " mixture strength, a min of 6·9 : 1 was found with a mixture 9% rich, and the usable C.R. then rose to 12·4 : 1 for a mixture 75% rich. Power output rose to maxima at " correct " mixture strength and at 40% rich, but varied by only 5% over the range 10% weak to 65% rich. H. C. E.

2268. Analysis of straight-run gasolines by means of the Raman effect. S. Mizushima, S. Nakamura, and T. Tobiyma. *Bull. Chem. Soc. Japan*, 1949, **22** (5), 213.—A brief account is given of the separation into fractions of straight-run gasolines (end point 150° C) from Sanga-Sanga, Rantau, Pentopo, Seria, and Miri, and the identification and determination of the components therein by the Raman spectra have been made. The components determined amount to 70–80% of the original gasoline. The remaining 30–20% corresponds to hydrocarbons whose spectra have not been reported. The compounds listed comprise : *iso*butane, *n*-butane, 2 : 2-dimethyl propane, *iso*-pentane, *n*-pentane, 2 : 2-dimethyl butane, *cyclo*pentane, 2 : 3-dimethyl butane, 2-methyl pentane, 3-methyl pentane, *n*-hexane, methyl *cyclo*pentane, 2 : 2-dimethyl pentane, benzene, *cyclo*hexane, 2 : 4-dimethyl pentane, 2 : 2 : 3-trimethyl butane, 3 : 3-dimethyl pentane, 2 : 3-dimethyl pentane, 2-methyl hexane, 3-methyl hexane, 3-ethyl pentane, *n*-heptane, 2 : 2 : 4-trimethyl pentane, methyl *cyclo*hexane, 1 : 2-

dimethyl *cyclo*pentane, toluene, 2 : 2 : 3-trimethyl pentane, 2 : 3 : 4-trimethyl pentane, 1 : 1-dimethyl *cyclo*hexane, 1 : 3-dimethyl *cyclo*hexane, 1 : 4-dimethyl *cyclo*hexane, 1 : 2-dimethyl *cyclo*hexane, *n*-octane, ethyl benzene, *o*-, *m*-, and *p*-xylene, *n*-nonane.
W. H. C.

Gas Oil and Fuel Oil.

2269. Comparative fuel values. A. H. Reed. *Fuel Oil & Oil Heat*, July 1950, **9** (7), 78.—Chart shows comparative fuel values based on equivalent heat units. Guide lines on top and bottom of chart if joined give the U.S. price of any selected fuel. Along the same line the comparative price of any of the fifteen fuels listed can be read.
D. K.

2270. The fuel, heat and power aspects of the petroleum chemicals plant for Petrochemicals, Ltd, Partington. E. Bonwitt and H. E. Charlton. *J. Inst. Fuel*, July 1950, **23** (132), 189.—Choice of fuel and the heat/power balance are discussed, and various alternative power and steam cycles compared. The reasons are listed for choosing oil in preference to coal as fuel for the Petrochemicals plant. The steam-raising plant has two unusual features; they are that the large water-boilers are installed in the open and that de-oiled condensate is used as feed water for high-pressure boilers. Electricity is generated in back-pressure turbo-alternators. Electrical distribution in flame-proof areas, problems of some heat- and power-consuming plants, and the costing system are discussed. Numerous diagrams are included. D. K.

2271. Oil burning. Tip-atomizing burners in the open-hearth furnace. A. L. Cude and J. R. Hall. *J. Iron & Steel Inst.*, Aug. 1950, **165** (4), 419–29.—Diagrams and descriptions are given of two types of tip-atomizing burners and of the modifications made to give control over atomization and flame shape. Tests carried out in an open-hearth steel furnace to compare the modifications with the original burners are recorded. High-speed cine-photography was employed in the tests, and photographs of the flames are given and described. Furnace performance, atomization and flame length, the furnace and its operation are described. Flame shape and burner maintenance are discussed. No significant differences in either furnace performance or fuel consumption were found. In all cases the same oil flow rates and steam oil ratios were required for smooth operation. It is suggested that the quantity of steam was the controlling factor in combustion, and that burner design was of minor importance. An appendix describes and illustrates steam–water jets from the second type burner. Details of the steam swirls and experimental data are given. W. H. C.

Lubricants.

2272. Powder metallurgy and lubrication. H. W. Greenwood. *Scientific Lubrication*, Apr. 1950, **2** (4), 2–4.—The directions in which powder metallurgy has contributed to the progress of lubrication are remarked, and the history, properties, and applications of porous or self-lubricating bearings are described. The control of pore size and the load-carrying capacity of porous bearings are discussed. Copper–lead bearings, the use of special coatings for bearing surfaces, and the applications of porosint filters are considered.
J. G. H.

2273. Role of cutting fluid as a lubricant. K. E. Bishopp, E. F. Lype, and S. Raynor. *Lubr. Engng*, Apr. 1950, **6** (2), 70–4.—The question of the existence of a continuous fluid film on the tool-chip interface in the metal-cutting operation is a controversial one. The problem is here considered theoretically, evaluating the pressure between the tool and chip, the temperature at the tool point, the viscosity of the cutting fluid at this pressure and temperature, the thickness of the fluid film for a given pressure, friction drag and viscosity, and the possible existence of a film whose thickness is thus determined. Considering oil, CO_2, Cl, and water as lubricating media it is concluded that, under the conditions postulated, a continuous lubricant film does not exist.
J. G. H.

2274. Relation between friction and adhesion. J. S. McFarlane and D. Tabor. *Proc. Roy. Soc.*, A, 7.7.50, **202** (1069), 244–52.—Simultaneous measurements have been made of the friction and adhesion of steel sliding on indium in air. The data show that both the normal and tangential stresses play a part in the deformation of the metallic junctions formed at the interface. When the surfaces are first placed in contact, a minute tangential force is required to initiate relative motion between the slider and the indium surface, since the junctions are already plastic under the applied load. As relative motion proceeds, the region of contact grows with a corresponding increase in the tangential force and the adhesive force. An upper steady state is reached where the tangential force increases more rapidly than the rate of growth of the region of contact and sliding on a macroscopic scale occurs. The detailed behaviour of the junctions during the early stages of the sliding process may be expressed quantitatively in terms of von Mises's criterion for plastic deformation under combined normal and tangential stresses, and there is good agreement between the theoretical relation and the experimental observations. The results emphasize the reality of the cold-welding process which occurs at the points of intimate contact when metal surfaces are placed together. The metallic junctions so formed are responsible both for the friction and the adhesion observed. Lubricant films diminish the amount of metallic contact, and so lead to a reduction in the friction and adhesion. W. H. C.

2275. Viscosity–temperature–pressure relationships of lubricating oils. R. I. Sanderson. *Lubr. Engng*, Dec. 1949, **5**, 283–7.—The significance of pressure and temp variations in visc as a means of predicting the performance of lubricating oils in service is remarked, and V.I., A.S.T.M. slope and relative viscosity–temp number are discussed together with the relations between pressure and viscosity. J. G. H.

2276. Laboratory wear tests for gear lubricants. S. A. McKee, J. F. Swindelles, H. S. White, and W. Mountjoy. *Scientific Lubrication*, Jan. 1950, **21**, 12.—A method is described whereby the S.A.E. E.P. lubricants testing machine can be adapted to measure accurately the wear obtained with various automotive gear lubricants under simulated service conditions. Points discussed include the rate of wear during the run-in period, surface roughness of the test cups, and the effects of chemically active additives. J. G. H.

2277. Delivery tests for the lubricant consumer. E. S. Jones. *Scientific Lubrication*, Apr. 1950, **2** (4), 15–16.—The importance of simple tests as a means of checking roughly deliveries of lubricants is remarked, and notes are presented on the general significance of colour and odour and of simple visc tests. Special tests applicable to cutting oils, neat cutting and drawing oils, quenching and tempering oils, rust preventives, and grease are briefly indicated. J. G. H.

2278. Molykote—a new lubricant. Anon. *Scientific Lubrication*, Apr. 1950, **2** (4), 16.—Molykote, claimed to have valuable properties as a dry lubricant and anti-seizing compound, consists of a smooth-textured molybdenum disulphide powder. Its uses as a breaking-in lubricant are remarked and its physical properties detailed. J. G. H.

2279. Draft of [specification] DIN 6553, refrigerator oils. H. Steinle. *Erdöl u. Kohle*, 1950, **3**, 334–6.—A revision of the specification last issued in 1933 is put forward based on requirements of modern refrigerators. Oils are divided into three classes, depending on nature of refrigerant, for use with (*a*) CO_2, NH_3, (*b*) SO_2, and (*c*) hydrocarbons and their Cl and F derivatives. Respective visc limits (cs) at 20 and 50° C are: 33–76, 10–17; 76–150, 17–28; > 150, > 33. Other requirements, common to all grades, include flash $\not< 150°$ C, pour $\not> -25°$ C (a U-tube type of cold test at the same temp is also specified), water $\not> 0{\cdot}003\%$ (determined by P_2O_5). Resistance to refrigerant and refrigerant-insol are determined by the Philipp test (*Kältetechnik*, 1949, **1**, 14) and the Frigen-12 method (*ibid.*, 1949, **1**, 87) respectively. The reasons for the various requirements are discussed. V. B.

2280. Lubrication servicing system. O. M. Albl. *Lubr. Engng*, Apr. 1950, **6** (2), 67–9.—Details are presented of the lubrication organization set up in a metal-

working plant. Points covered include selection and testing of lubricants, scheduling of lubrication routine, and identification of types of lubricants with points of application. J. G. H.

2281. Some new E.P. lubricating oil additives. W. Davey. *Scientific Lubrication*, Jan. 1950, **2** (1), 2.—Data are presented on the preparation of chlorbutol compounds (sulphides and disulphides) for use as E.P. additives. Properties and test results are summarized, and it is concluded that, while not suitable for commercial development, these compounds furnish useful information for the preparation of improved additives. J. G. H.

2282. Steam turbine lubrication. W. E. J. Broom and G. H. Clarke. *Scientific Lubrication*, Jan. 1950, **2** (1), 7–9.—The lubrication system of the modern steam-turbine is described, and the properties required in a turbine oil are enumerated. Oxidation, secondary corrosion, and rust inhibitors are discussed, together with the interfacial tension test and the use of centrifuging to extend oil life. J. G. H.

2283. Lubrication of marine turbines. F. S. Jones. *Scientific Lubrication*, Apr. 1950, **2** (4), 8–12.—The three commonly used lubrication systems for marine turbines—gravity, pressure, and gravity-pressure systems—are briefly described, and fundamental design data common to these are discussed, together with design features of the propulsion equipment which may contribute to the elimination of possible contamination. Details are presented of measures adopted to keep equipment free from rust and dirt until the regular turbine oil can take over this function. The cleaning procedure for new installations and the operation of charging with new oil are described in some detail. J. G. H.

2284. Diesel engine lubrication problems when using high-sulphur fuels. E. H. Kadmer and K. H. Lüers. *Erdöl u. Kohle*, 1950, **3**, 266–71.—Lubrication of C.I. engines presents a different problem to that of spark-ignition engines. 4000-km test on a Mercedes engine using an Arabian acid-refined mixed-base oil gave good results, indicating appreciable detergent effect. Noack ageing test (1 hr at 250° C, removal of oil vapours during test, under a 40 mm vac, determine oil const, including visc and asphalt) was carried out on a number of oils; results indicate that dist raffinates gave better results alone than when blended with bright stock, unless latter had been freed from resin. Use of fatty oils in blends is strongly contra-indicated. Rise of visc alone is not a criterion of ageing, since it is largely due to evaporation losses under the test conditions. Better indication is obtained by observing visc rise on vac dist to same % residual oil; ratio of these visc rises indicates thickening of oil that is due to oxidn. Oil analyses after various bench and road tests are given. Visc of new oil should be $> 10^{\circ}$ E_{50}. Results of Kern (cf. Abstract No. 1032, 1939) are reproduced and discussed in light of present-day knowledge. His tests show that use of a fuel containing 0·74% S approx doubles soot, ash, and asphalt content of oil as compared with fuel of 0·34% S. It is suggested that, with help of additives, an S content in the fuel of up to 1·3% can be tolerated. V. B.

2285. Lubrication of ball and roller bearings. T. B. Sansom. *Petroleum*, May 1950, **13** (5), 112–13.—The principles of lubrication and the functions of lubricants are outlined, including the importance of fluid friction caused by movement of the lubricant. Danger of over-lubrication is pointed out.

Lime-base greases are suitable only for low-speed and low-temp applications, soda-base greases are suitable for most general purposes with normal temps and at speeds not exceeding 3000 r.p.m., but for high-speed work, oil is the best form of lubricant. Methods of applying and replenishing lubricants are briefly discussed. The American " New Departure " bearing, which is self-sealed and lubricated, is described. R. E. P.

2286. Grease. E. A. Evans. *J. Inst. Petrol.*, 1950, **36**, 367–77.—A brief history of the development of lubricating greases and their testing is given. Information is presented on the factors influencing fibre formation in metal soap–mineral oil systems. A. R. W. B.

2287. New approach to lubricating grease structure. G. V. Browning. *Institute Spokesman*, Apr. 1950, **14** (1), 10–15.—The effect of solvents on oil–soap systems has been studied, and results obtained have facilitated the development of experimental techniques whereby the application of solvents to greases can be used to study their structure. Copious amounts of solvents will dilute the oil in a grease without disturbing the soap structure so that the grease will regain its original form on evaporation of the solvent. Also, the oil in a grease can be extracted by a solvent and replaced, without the loss of grease characteristics, by addition of the second oil or other liquid to the solvent–soap system before the solvent is permitted to evaporate. The application of these techniques to the study of grease structure is discussed, and suggestions for future work on the subject are outlined. J. G. H.

2288. Grease symposium. American Society of Lubricating Engineers. *Lubr. Engng*, Dec. 1949, **5**, 270–82.—A series of short papers on greases and grease-lubricating systems, the use of grease in anti-friction bearings, machine tools, mining machinery, and the steel industry. J. G. H.

2289. Twister ring greases. I. G. Roehner, E. S. Carmichael, and F. S. Jones. *Institute Spokesman*, Jan. 1950, **13** (10), 10–16.—The mechanism employed for yarn twisting in the textile industry is briefly indicated, and the functions of ring and traveller in connexion with lubrication are outlined. The types of greases used for light and heavy duty twisting are enumerated, and flow properties, chemical stability, film strength, ease of application, colour, and odour are discussed as significant characteristics. Details are presented of a functional tester for the laboratory evaluation of twister-ring greases which indicates relative flow and film-strength properties by means of traveller wear data. J. G. H.

2290. It's the chemist who changes your oil. Anon. *Laboratory*, 1950, **19** (5), 99.—A general review is given of the subject of additives in lubricating oils. In the last twenty years, the additive industry has increased to an annual production valued at *ca* $40 m. The various types of lubricating-oil additives are described, and an account of their modes of action is given. Some economic aspects of additive development are briefly considered. C. N. T.

2291. Military raises standards for heavy-duty motor oils. Anon. *Petrol. Process.*, 1950, **5** (5), 475–6.—Changes in the U.S. Armed Services specifications for heavy duty engine oils announced at the Lubricating Oil Discussion Panel during the Mid-Year Meeting of the National Petroleum Assn. in Cleveland, April, 1950 are reviewed. New oils must be capable of satisfactory service with the higher-sulphur-content fuels expected to be in greater use in the future. The main change is in the sulphur content of the fuel used in the heavy duty engine oil-test procedure. The existing test fuel specification for a natural sulphur content of 0·4% max is to be changed to a min of 0·35%. D. W. F.

Bitumen, Asphalt, and Tar.

2292. Viscosity of Bitumens. N. N. Korotkevich. *Petroleum*, Mar. 1950, **13** (3), 63–5. (*Translated from symposium on the viscosity of liquids and colloidal solutions, Academy of Sciences of U.S.S.R.*)—Describes theory and practice of bitumen visc determination. An apparatus, using rotating cylinders based on a design by Volarovich, has been used for investigating the visc of asphaltic road bitumens. Electrical heating and temp control were employed. It was shown that the absolute visc of bitumen changes very sharply with temp, and that bitumen when fluid behaves as a Newtonian fluid. R. E. P.

2293. The handling of submersing mattresses made from bituminized sand. E. Kuiper. *Ingenieur*, 28.7.50, **62** (30), B-89.—In connexion with the building of a harbour embankment at Harlingen, in Holland, the " mattress " or carpet is composed of 18% wt bitumen, 10% wt filling, and 72% wt graded sand, the whole being reinforced with a rope mat. R. R.

Special Hydrocarbon Products.

2294. Non-flammable hydraulic fluids—2. C. M. Murphy and W. A. Zisman. *Lubr. Engng*, Dec. 1949, **5**, 264–9, 304.—The properties are discussed of glycols, silicones, chlorinated and fluorinated compounds, and aqueous solutions as hydraulic fluids, with particular emphasis on pump wear and on the action of packings. Hydrolube U-4 is considered promising, and there are possibilities in perfluorinated hydrocarbons, ethers, and amines. An extensive bibliography is included. J. G. H.

Derived Chemical Products.

2295. Heats of transition of hexachloroethane. S. Seki and M. Momotani. *Bull. Chem. Soc. Japan*, May 1950, **23** (1), 30–1.—The heats of transition of hexachloroethane have been determined by direct specific-heat measurements. The transition points are 45° C, for the triclinic⟷monoclinic and 72° C for the monoclinic⟷cubic, modifications. Since the transition at 45° C was frequently found to be superheated, to avoid this the specific heat was measured as slowly as possible in a specially constructed calorimeter. The observed magnitude of the heat of transition (ΔH) was found to be 613 cal/mol at 45° C, and 1956 cal/mol at 71·4° C. Both results are in good agreement with the results from vapour-pressure measurements by the other observers indicated. Entropy change (ΔS) at the transition point is 1·93 E.U. at 45° C, and 28·0 E.U. at 71·4° C. The change at 71·4° C is greater than the change at the melting point (185° C) reported by van de Lee, viz., 5·50 E.U. Volume change (ΔV) at transition point is 9·7 cc/kg at 45° C, and 28·0 cc/kg at 71·4° C, shows a very good parallelism between entropy and volume change at these transition points. W. H. C.

2296. Styrene—a historical survey. F. Armitage. *Petroleum*, Apr. 1950, **13** (4), 87–90.—An account is given of the development of styrene as a commercial product from its discovery to the present day. Its preparation and methods of manufacture, its reactions, including methods of polymerization, and its applications are outlined. Styrene is being obtained in increasing amounts from by-products of the petroleum industry.

Increasing interest is now shown in styrene containing surface coatings, styrenated-oil paints, and styrenated-alkyds. Copolymers formed with other unsaturated materials show various modification in properties, and are suitable for different applications—water and chemical-resistant lacquers, fabric impregnation, printing inks, and moulding plastics. R. E. P.

2297. Pure hydrocarbons from petroleum—recovery of aniline solvent from Distex hydrocarbon products by water extraction. J. Griswold, J. Chew, and M. E. Klecka. *Industr. Engng Chem.*, 1950, **42** (6), 1246–57.—Liquid-phase equilibria for the ternary systems formed by aniline and water and each of the hydrocarbons *n*-heptane, methyl*cyclo*hexane, and benzene at 25° and 50° C are presented. Three conjugate phases occur in the *n*-heptane and methyl*cyclo*hexane systems at both temps. Separate hydrocarbon and aniline phases do not appear in the benzene system. Application to design of extractor to recover aniline from Distex hydrocarbon streams by water scrubbing and to extract aniline from aqueous solutions by a hydrocarbon wash is discussed. Complete removal of aniline by water washing is shown to be possible. R. G. T.

Coal, Shale, and Peat.

2298. High pressure hydrogenation of carbonaceous matter. Part I. Introduction. P. W. Sherwood. *Refiner*, 1949, **28** (12), 97–101.—The increase in consumption of hydrocarbon products and the relative decline in petroleum discoveries in the U.S.A. combine to make the economic outlook for synthetic fuels more attractive. Natural gas would provide an excellent basis for production, but estimated reserves limit its long-term application. It is estimated that coal constitutes 98·8% of the total fuel reserves of the U.S.A. A synthetic fuel industry based on coal could use Fischer–

Tropsch or hydrogenation processes. Fischer–Tropsch product is mainly straight-chained paraffins and olefins. High-pressure hydrogenation gives a highly aromatic product. Germany has twelve synthetic fuel plants; Czechoslovakia, one; England, two (Billingham and Heysham); Japan, one; Italy, two; Spain, two contracted. The development of high-pressure hydrogenation and catalysts is described. A flow diagram and description outlines the process. R. W. G.

2299. High pressure hydrogenation of carbonaceous matter. Part II. Primary hydrogenation in the liquid phase. P. W. Sherwood. *Refiner*, 1950, **29** (1), 119–23.—When coal is heated to 750° F a breakdown of molecular structure occurs. The exact mechanism is not clearly understood, but it is thought that the products tend to polymerize. The presence of hydrogen minimizes this polymerization. Solvents are used which are capable of giving up hydrogen to the coal, and a satisfactory solvent has been found in the oil produced by hydrogenation. It has been found that any gasoline produced in the liquid-phase hydrogenation has poor engine characteristics, and that it is preferable to produce middle oils at this stage and from these to obtain gasoline in the vapour-phase hydrogenation.

The suitability of a coal for hydrogenation depends mainly on its composition, and the various properties favourable to hydrogenation are listed. Suitable catalysts are dependent on the pressure used and the type of coal. Patented catalysts cover almost the whole periodic table. Some known successful catalysts are given, and the required performance limits of catalysts are described. Mild air oxidation of high carbon content has been used in Germany to improve the raw material. Lowering of the ash content beforehand saves its removal later. The coal is usually ground to pass a 65 mesh (Tyler scale). R. W. G.

2300. High pressure hydrogenation of carbonaceous matter. Part III. Primary hydrogenation in the liquid phase (contd.). P. W. Sherwood. *Refiner*, 1950, **29** (2), 106–10.—The effect of operating variables. Not only is the addition of a vehicle to coal a mechanical advantage, but also it has a favourable effect on the conversion. Increase in contact time or increase in temp affect the product distribution, an increase in either tending to give a lighter product. Industrial practice is limited to a temp of 860–920° F by space performance and coke formation. Coke formation increases with increased temperature, but can be counteracted with higher pressures. At least 3000 p.s.i. is needed, and normal practice for young coals is 4400 p.s.i. and 10,300 p.s.i. for a bituminous coal. Typical rate for 10,300 p.s.i. pressure is 1·2 tons/hr per hundred cu. ft. of reactor volume and 0·8 for 4400 p.s.i. Contact time is about 1·2 hr. Due to the low catalyst concentration, the products of liquid-phase conversion are related to the raw material. The quantity of gaseous products is affected by operating conditions. As by-products, many of the hydrocarbons in the asphalt have potential value. Tar acids are present in the oils, roughly 1 ton of bituminous coal will yield 30 lb of phenol and 70 lb of cresols and xylenols. Liquid-phase gasoline also contains recoverable chemicals, *e.g.*, acetone, methyl ethyl ketone. R. W. G.

2301. High pressure hydrogenation of carbonaceous matter. Part IV. The liquid phase in industry. P. W. Sherwood. *Refiner*, 1950, **29** (3), 150–4.—The amounts of raw materials required are tabulated for various starting materials. Preparation of the coal is carried out in standard milling plant. Steam conversion of water gas (from coal, coke, or by-product methane) is used to produce the hydrogen. Hydrogen production from coal represents 30% of the total hydrogenation process costs. The various pump requirements are described. High-pressure vessels are contained in three-sided "stalls." Converters are constructed of chrome–nickel–molybdenum low-alloy steel protected from high temperatures by insulation. They are either integral forgings or "ribbon wound" vessels. Regenerative tube and shell heat exchangers are used. Although reaction is exothermic, a preheater furnace is required and is the most expensive piece of equipment. To avoid erosive effects and possible coking the preheater consists of a single tube mounted vertically. Radiant heat transfer is avoided, and coefficients range from 1·5 to 2·5 B.Th.U/sq. ft/hr/° F. The hot catch pot separates slurry from the gaseous products, and care had to be taken to prevent coke formation at this point. Emergency release towers are situated some distance from the plant. Automatic control is desirable, and with it labour can be

reduced to 1–1½ men per shift per stall. Due to the precautions taken, the incidence of industrial accidents in high-pressure plants is lower than that in the chemical process industry. R. W. G.

2302. High pressure hydrogenation of carbonaceous matter. Part V. The liquid phase in industry (contd.). P. W. Sherwood. *Refiner*, 1950, **29** (5), 123–7.—At present, residue processing is probably the crux of the hydrogenation process. Many methods have been tried and other methods are in the course of development, but the present industrial practice is centrifuging followed by carbonization. A typical residue is 20–27% benzene-insoluble matter and 18% asphalt, mean particle size of solids being 1·5μ. For centrifuging, residue is diluted with some of the bottom products of the primary distillation of the oils. Carbonization is carried out in worm- or ball-type retorts, this unfortunately incurring high maintenance charges due to the short life (1–4 months) of the furnace liners.

Heavy oils are separated from the middle and gas oil fractions by distillation in conventional columns, although the packed type is usually preferred, less trouble being caused by coking. In German plants all overheads are taken to vapour-phase hydrogenation. The Billingham plant, however, separates the gasoline in a second column.

Mild operation of the hydrogenation process, aimed at the production of fuel oils, gives a high yield of gasoline, since gas formation is low.

Processes under study are the steam flashing of the residue, a combined hydrogenation and distillation plant, conversion of the coal to methane; hydrogenation of powdered coal in a fluidized bed. R. W. G.

2303. High pressure hydrogenation of carbonaceous matter. Part VI. The vapour phase in industry (Section A). P. W. Sherwood. *Refiner*, 1950, **29** (6), 113–17.—The principle function of the vapour-phase hydrogenation is to convert the higher-boiling oils into gasoline. Unlike thermal and catalytic processes, if so desired gasoline only can be produced. Usually the process is carried out in two stages. First, the pre-saturation stage, the function of which is primarily to remove objectionable basic nitrogen or phenolic oxygen. It is carried out under mild operating conditions (720–750° F, 4400 p.s.i.) using a tungsten sulphide catalyst. If appreciable quantities of gasoline are formed, these must be removed by distillation before the vapour-splitting stage. The reaction is exothermic, 1 lb of oil resulting in the evolution of 180–270 B.Th.U. This is followed by a water-scrubbing stage to remove ammonia. Typical operating conditions for the splitting stage are 750–790° F and 4400 p.s.i. A 73–74 (Motor Method) octane number gasoline is produced. Catalyst used is tungsten disulphide and fullet's earth. This catalyst requires a minimum sulphur content of 2% and if necessary hydrogen sulphide is used. R. W. G.

2304. Estimating oil yield of oil shale from its specific gravity. I. C. Frost and K. E. Stanfield. *Anal. Chem.*, 1950, **22**, 491–2.—The specific gravity of oil shale may be used as a rapid and practical method of estimating the oil yield from a given source. It has been shown that a relationship existed between the oil yields of shales from the same source determined by the modified Fischer assay method and their specific gravities, and this oil-yield–specific-gravity relationship provides a means of estimating the oil yields of similar shales from the same source. However, this numerical relationship was not the same for shales from different sources, but it was shown that a similar relationship existed for these shales. This method of estimating oil yield of shales may be adapted to rapid routine testing where time and equipment will not allow essays to be made by the more reliable modified Fischer-retort assay method. J. S.

2305. Underground carbonization of oil-shale. A. Schneiders. *Erdöl u Kohle*, 1950, **3**, 330–3.—Normal processing of shale involves loss of about 30% of available heat content of shale and considerable labour in mining, thus preventing exploitation of low-grade deposits. Description is given of the Holzheim process for carbonizing shale *in situ* underground. Drifts are driven into shale deposit, leaving intermediate pillars of shale rock, these pillars being pierced with holes for pipes supplying air and steam. Shale pillars are processed in groups of six, the cycle being preheating, heating to 100° C, drying, carbonization, combustion, glowing to exhaustion. Air introduced for combustion stage is preheated by last pillar of the series. Flow diagram is given.

Combustion gases issue from workings separately from the oil vapours. Process enables 80% of the shale to be utilized underground, remaining 20% being removed to make the necessary workings. This latter shale is utilized on surface in special oven to generate steam required for the underground distillation, and also to yield oil.
V. B.

2306. New shale oil refinery. B. Guthrie and R. J. Cameron. *Petroleum*, Feb. 1950, **13** (2), 36–8.—A summary of the paper "Oil shale as a supplement to petroleum" presented before the Independant Petroleum Association of America. Reserves of oil shale dwarf present known reserves of petroleum. To recover the oil the shale must be heated to 850° F to thermally decompose the solid, insoluble organic kerogen. Retorting may be carried out simply by heating, passing hot gas through beds of broken shale, or using the fluidized-solids technique of fluid catalytic cracking.

Oils produced are compared with a typical mid-continent petroleum crude. The naphtha is 50% olefinic, and contains less than 4% gasoline, hence significant quantities of light distillate products must be produced by thermal or catalytic cracking. Further treatment to remove tar acids, tar bases, and sulphur is conventional.

A refinery, capacity 300 b.d., has been put into operation at Rifle, Colorado. It is capable of straight distillation, coking, thermal cracking, and reforming Products will be petrol, diesel fuel, heating oils, butane–propane, and fuel gas. There is also the possibility of chemical by-products such as phenol and pyridine from the tar acids and bases.

Catalytic cracking produces high-quality gasoline, but present catalysts are eventually poisoned by nitrogen compounds. Hydrogenation appears very suitable, as it improves carbon–hydrogen balance and removes nitrogen and sulphur. Gasoline from destructive hydrogenation should be of aviation quality. R. E. P.

Miscellaneous Products.

2307. Aliphatic petroleum naphthas in industry. Part I. H. N. Frost. *Refiner*, 1950, **29** (2), 95–9.—The oil-refining industry is being called on to provide more and more compounds and groups of compounds to fulfil the requirements of other industries. The first part of this series describes the requirements of the principal consumers, viz.: the protective-coating industry, which is chiefly concerned with the volatility and solvency of the product; the rubber industry, which is concerned with the volatility, flash point, and freedom from olefinic or unsaturated compounds; and solvent extraction and other miscellaneous industries. By understanding the needs of their consumers the oil-refining industry will be able to assist these consumers.
R. W. G.

2308. The assay of stocks for aliphatic naphtha production. Part II. H. N. Frost. *Refiner*, 1950, **29** (3), 135–9.—To meet the growing demand for specialty naphthas, refiners re-examined their crude stocks to see whether they could be used. The crudes were fractionated in the laboratory to close-boiling-point fractions then blended as follows: I.B.P. to 250° F, 250–300° F, 300–400° F. Aniline number, solvency, flash, sulphur content, and other tests were carried out to indicate whether a particular crude would be suitable. The results for various crudes are tabulated. The distillation was carried out in an Oldershaw glass bubble-plate column having seventy-five plates. This column and controls are described. R. W. G.

2309. Manufacture of aliphatic petroleum naphthas. Part III. H. N. Frost. *Refiner*, 1950, **29** (4), 137–40.—A modern naphtha-fractionating unit has been constructed. The primary column has sixty-six bubble trays, the secondary column sixty-five trays. Reboiler heating and feed preheating is carried out by hot-oil circulation. The bottoms from the primary tower are fed into the secondary. Because of the close-boiling fractions required, the unit is controlled entirely by constant flow. To obtain high yields by this method feed composition must be constant. Volume data from the analytical distillation is invaluable for calculating flow rates required. Six alternate feed inlets on primary and secondary columns allow for the use of varying feed stocks and the production of various products. R. W. G.

2310. Pyrocatechol from low-temperature tar. W. Lowenstein-Lom. *Petroleum*, Mar. 1950, **13** (3), 61–2.—A new process is described. Phenosolvan, a mixture mainly of *iso*butyl acetate, of *n*-butyl and amyl acetates, is used for the extraction of low-temp carbonization effluents rich in pyrocatechol. Further processing of the phenosolvan extract, from which the solvent has been removed by distillation, consists primarily of a vacuum batch distillation, of which details are given. The pyrocatechol fraction obtained is then purified by recrystallization from benzole; a purification plant is described. Other fractions obtained can be worked up for phenol and cresols.

The purified product contains 4–8% homologues, but a further recrystallization brings it to 99·2% purity. However, the less-pure product can be used as a base for synthetic tanning agents or for plastics, as a stabilizer for polystyrene and polymer gasolines, for the manufacture of special plasticizers, azo-dyes, etc.

Costs of production are small compared with synthetic production, and compare favourably with present market prices. R. E. P.

2311. Detergents of the future. A. L. Fox. *Soap Sanitary Chem.*, June 1950, **26** (6), 37.—It is probable that, in the future, improvements in synthetic detergents will fall into the following three groups :—

1. Improvements in the conventional type detergent of to-day.
2. Improvements through adding properties not possessed by synthetic detergents.
3. Changes in physical form.

As regards active material, it is likely that non-ionic detergents with improved foaming properties will be the most immediate development. The question of builders is coming very much to the fore at present, and in the next fifty years it can be expected that detergent powders specially built for particular applications will make their appearance.

It is predicted that detergents in liquid form will soon come into competition with those in the powder form. O. M.

2312. Methods of evaluating detergents. C. T. Snell. *Amer. Dyestuff Rept.*, 1950, **39** (15), 485.—The general nature of synthetic detergents is briefly reviewed. The various detergent-evaluation methods considered include measurements of surface and interfacial tension, dispersing and wetting power, and finally, actual washing tests simulating as closely as possible practical conditions. C. N. T.

2313. Soap and detergents as affecting textiles. F. D. Snell. *Amer. Dyestuff Rept.*, 1950, **39** (15), 481.—The general principles of detergency and wetting are discussed, and the salient advantages and disadvantages of the various surfactant types outlined. The effect of various fabrics, the washing ability of various fabrics, and the washing ability of soaps and synthetic detergents are compared. Other textile applications of these products are considered. C. N. T.

2314. Synthetic plastics, fibres and rubbers—from petroleum. E. V. Murphree. *Oil Gas J.*, 27.7.50, **49** (12), 222.—A review is given of the synthetics made from petroleum. Method of production, properties, and uses of the various products are outlined, figures show steps in syntheses, and typical products from ethylene and intermediate form aromatics are listed. G. A. C.

2315. Tint retention of coloured paints based on white pigments. C. T. Morley-Smith. *J. Oil & Col. Chem. Assoc.*, June 1950, **33** (360), 249.—A series of exposure tests to investigate the comparative resistance to fading of coloured paints based on different white pigments was carried out at six dissimilar sites in Great Britain.

Results were recorded by shade-card comparisons, photo-electric measurements, and colour photographs and showed zinc oxide and lithopone to be much superior in tint retention to antimony oxide, rutile and anatase titanium dioxide, and white lead.

Results are discussed in relation to varying conditions prevailing at the six sites, and to the different ultra-violet absorption of pigments concerned. Loss of colour can be attributed to three causes : change in the colouring pigment itself, by chemical

breakdown or interaction, masking of colour by a change in the paint film, or masking of the colour by adherent dirt. It is concluded that behaviour towards ultra-violet rays of the sun's spectrum is not the only factor contributing to the protection a white pigment can give against fading in a coloured paint. The role played by moisture may be significant. Many figures and plates are included. There are eight literature references. D. K.

2316. Heat treatment of oils and resins for paint and varnish making. Anon. *Paint Mfr.*, Aug. 1950, **20** (8), 286.—Report is issued by the North Thames Gas Board. The reasons for heat treatment are discussed. For the purpose of heat treatment materials used in the manufacture of paints and varnishes may be classified as drying oils, non-drying oils, and fossil resins. A table is given of the temps required to produce the desired properties in various materials. The equipment for oil heating, gum running, oil boiling, non-drying oils, varnish making, etc., is described, and many diagrams are included. D. K.

2317. Piperonyl butoxide in low pressure aerosol insecticides. H. O. Schroeder. *Soap*, June 1950, **26** (6), 145.—Piperonyl butoxide is most generally acclaimed by reason of its ability to increase the " knock-down " properties of pyrethrum sprays and because it is effective in such a large range of concentrations. Therefore its remarkable degree of synergism in terms of mortality is less well known. The fact that it does not present any toxic hazards makes it all the more attractive.

The results of an investigation of sprays containing pyrethrum and piperonyl butoxide are given. O. M.

2318. Automatic transmission fluid—type A, for passenger cars. H. R. Wolf and J. L. McCloud. *Refiner*, 1950, **29** (4), 153–6.—With the increase in production of auto-transmission units it has been suggested that, for refilling or servicing, one type of fluid be produced. The required properties of such a fluid are listed. While one or more of these properties may not be necessary for a particular manufacturer's transmission unit the resulting fluid should be satisfactory in any unit. Hence it becomes an advantage to equipment manufacturers, fluid-servicing stations, petroleum marketers, and the car owner, besides avoiding costly failure due to the use of an incorrect fluid. R. W. G.

CORROSION.

2319. Corrosion problems in gas purification units employing M.E.A. solutions. F. E. Riesenfeld and C. L. Blohm. *Refiner*, 1950, **29** (4), 141–50.—It has been observed that rather severe corrosion occurs in plants employing aqueous solutions of mono-ethanolamine for the removal of carbon dioxide from flue gas. This is considered to be due to the carbon dioxide (as well as electrolytic action, etc.), and not due to the formation of organic acids as has been previously thought. Hydrogen sulphide aggravates the attack by precipitating any dissolved iron as the sulphide. Extensive tests support this theory while comparing both qualitatively and quantitatively the rate of corrosion of carbon, nickel, stainless, and Cr–Mo steels and aluminium alloys. The carbon and nickel steels showed the worst corrosion. Increasing percentages of diethylene glycol decrease the rate of corrosion of aluminium alloys and aluminium–steel couples. R. W. G.

2320. Design of cathodic protection for open-box type coolers. C. R. Draughon and E. B. McNeil. *Refiner*, 1950, **29** (5), 97–104.—(*Mid-year mtng of A.P.I's divn of refining, Cleveland, Ohio.*)—Many open-box-type coolers are still in service, often using muddy river-water or seawater as a coolant. Consequently, corrosion presents a serious problem. At Baton Rouge Refinery, experiments in cathodic prevention of the corrosion in such a plant have been carried out. One unit which has been in service with experimental cathodic protection apparatus will be inspected after two years. As pipes were two years old when protection was installed, this is eighteen months longer than life of pipes without protection. Two further units have been

equipped with cathodic protection, and results appear satisfactory. A rectifier provides 75 amp at 12 V D.C. to anodes, made from 1-in-dia carbon-steel reinforcing rods.

Photographs and figures illustrate the unit, and wiring system and details such as current density, potentials near the pipes and walls, etc., are given.

R. W. G.

2321. When and how to line process vessels with stainless steel. R. G. Sloan. *Chem. Engng*, 1950, **57** (3), 117–21.—The relative merits of solid, clad, and lined stainless-steel vessels are related to wall thickness. $< 0{\cdot}25$-in solid; $0{\cdot}25$–$0{\cdot}5$-in solid and stainless-clad compete; $0{\cdot}5$–$1{\cdot}0$-in clad and lined compete; $> 1{\cdot}0$-in stainless lined are usually most economical. In cases of severely corrosive liquids solid stainless is best up to $0{\cdot}75$ in.

Details of the execution and relative merits of plug welding, one-, two- and three-bead butt welding, butt strap, and lap welding the linings are given.

Cleaning by sand blasting and testing with soap solution are recommended.

D. H.

2322. Corrosion on new distillation unit processing low sulphur crude. D. L. Burns. *Corrosion*, 1950, **6** (6), 169.—The case history of corrosion experienced on a new atmospheric and vacuum crude distillation is presented. The crude charged had a sulphur content averaging $0{\cdot}20\%$, and was produced in West Texas mostly from Ellenburger formations, of Ordovician age. Some test data for this crude, which are applicable to the corrosion problems are tabulated for comparative purposes with like data for two other crudes from Texas. A simplified flow diagram, temp and pressure conditions, and materials used in various items of equipment are given.

The parts most affected by corrosion were the atmospheric tower, overhead condenser shells, and the carbon steel tubes in the radiant section of the fired heater, where desalted crude is heated to 600° F. Ammonia injection was used in neutralizing the corrosive elements in the atmospheric tower overhead steam. Alloy steel tubes of 7% chromium and $0{\cdot}5\%$ molybdenum were substituted for carbon steel in the radiant section of the furnace. Corrosion rates for the carbon-steel heater tubes are plotted against temp and compared to those experienced when processing West Texas crude containing $1{\cdot}5\%$ sulphur as well as a topped high-sulphur crude. It is shown that the percentage of sulphur in a crude is not a direct measure of its tendency to corrode and that a low-sulphur crude may be extremely corrosive to carbon-steel furnace tubes of a distillation unit under certain conditions. The corrosion rates in the tubes in the crude heater processing Ordovician crude were severe, above 550° F, and very sensitive to oil-film or tube-wall temp. The same crude which gave trouble on the new unit had been processed previously in an older, though similar, unit for about three years without corrosion difficulties. A comparison between the operating data for the two units is given.

J. T.

Engines and Automotive Equipment.

2323. Automobile test rigs. L. H. Dawtrey. *Auto Engr*, July 1950, **40** (529), 259.—The paper begins with definitions of the word "rig," and a description is given of the background of automobile rig testing. Descriptions and illustrations are given of typical rig test equipment which reveal how essential it is for the machines to be versatile and capable of being altered easily for various widely different jobs.

A. S.

2324. Automobile test rigs. L. H. Dawtrey. *Auto Engr*, Aug. 1950, **40** (530), 286.—Continuing the paper started in the July issue (p. 259) a description is given of synchromesh gear-wear tests. A "life" before the onset of "crashing" gears under the severe conditions listed is around 30,000 gear changes. A photograph illustrates a rear-axle test house, and the method of testing is given. A useful rig which is being more widely used in experimental shops is the flow rig, for measuring air flow, particularly for inlet and exhaust passages of poppet-valve engines. It is most valuable

in the development of ports and manifolds. A shock-absorber or suspension-damper " carding " rig is described. It is also shown how hot-fatigue tests are carried out on valve steels to examine the suggestion that " XB " exhaust-valve steel is weak at high temps. Finally, an accelerometer rig is described which is used in the calculation of vehicle performance. It is a liquid type using an inclined tube similar to an inclined-tube manometer, and a tap to adjust damping and to cut off when not in use. Together with this is described a method of measuring instantaneous speed by using a fifth wheel to drive a Hasler tachometer. A. S.

2325. Directional stability. C. E. Lind Walker. *Auto Engr*, Aug. 1950, **40** (530), 281.—The paper consists of a summary of the findings of a design investigation into the method of securing stability in a new design. The project under consideration was a small ultra-light car. Because of the high frontal area to weight-ratio air resistance will form a greater proportion of total resistance for smaller car than for larger type, even though latter may be faster. Recent French ultra-light cars have supported this theory by the fact that they are carefully streamlined even though they are not intended for high-speed use. Wind forces also affect directional stability, and small car might again be more seriously affected than large car. Greater ratio of laden/unladen weights may also make small car less stable upon its tyres than larger car under some conditions of loading. The question of ground stability is discussed in detail and also aerodynamic forces produced by a wind inclined to the path of travel of the car. Any trend towards lighter cars with smaller engines increases the importance of aerodynamic forces, since their magnitude can no longer be reduced in proportion to the weight. Special consideration must be given to shape of the body if drag is to be reduced without impairing directional stability. A. S.

2326. Running ships on heavy fuel. Anon. *Motor Ship*, Aug. 1950, **31** (367), 172.—Full description given of M.S. *Nottingham*, an 8600-ton, 15-knot refrigerated cargo-vessel for the Federal S.N.Co. Main engine is of standard Brown–Doxford, opposed-piston, all-welded design with six cylinders, having dia of 670 mm and combined piston stroke being 2320 mm. Arrangements made to run engine on heavy fuel, and a quantity already bunkered of 0·98 sp. gr., of visc 800 sec Redwood No. 1. Purifying equipment illustrated, and includes three De Laval machines of largest type, driven by 7½-h.p. motors, two being used as separators and third as a clarifier. A fourth De Laval separator deals with lubricating oil, and a fifth centrifugal machine of Titan type is used for purifying diesel fuel supplied to auxiliary generating sets. Heavy fuel is taken from wing bunker settling tanks, through steam-heaters to centrifugal separators, which supply purified fuel direct and without intermediate heating to clarifier, from where oil is supplied to two 15-ton ready-use tanks, and through heaters to main fuel-pumps. Steam-jacketed pipes take fuel from pumps to injectors, and final temperature is 150° F. On maiden voyage ship will bunker fuel of 400 sec Redwood No. 1 at Aden, this being only grade of heavy fuel available, but owners intend to run engine on Ordoil of 1500 sec visc, obtainable at Curaçao.

Large two-stroke-engined auxiliary generating sets are described and illustrated, and machinery plans of the ship shown, together with descriptions of deck equipment and acommodation. U. N.

2327. Investigations on cylinder-liner wear. W. J. Payne and W. F. Joachim. *S.A.E. Trans.*, Jan. 1949, **3** (1), 51–68.—U.S. Navy experience with marine diesel engines in cyl-liner wear investigation is reported. Engine factors found to have a pronounced effect on cylinder wear included bore size, piston speed, cyl displacement, b.e.m.p., liner hardness, piston-skirt clearance, fuel consumption, lubricating-oil consumption, lubricating-oil temp, and cooling-water temp. A new theory, that of surface-disintegration wear, is propounded to account for cyl-liner wear, and the results obtained with chromium plating are discussed. J. G. H.

2328. Open combustion-chamber diesel engines in Britain. G. B. Dicksee. *S.A.E. Trans.*, Jan. 1949, **3** (1), 89–106.—The factors leading to the predominance of the diesel engine in the heavy commercial and coach field are remarked, and characteristics of direct-injection and swirl-chamber engines are enumerated. The function of air swirl

in maintaining max combustion efficiency is discussed, and the nature of the air movement so obtained is described. Descriptive details are included of present-day British engines, with a note on the fuels used. J. G. H.

2329. New vee-eight high-speed diesel engine. Anon. *Gas Oil Pwr*, 1950, **45**, 122–5.—This Rover Meteorite light-weight engine has eight cylinders of dimensions 5·4 by 6 in in two banks inclined at 60°. The C.R. is 16·5 : 1, and the engine develops 320 b.h.p. at 2400 r.p.m. Constructional details are described.

Each cast Al cylinder-head is fitted with two inlet and one exhaust valves. The combustion chambers are of the Ricardo Comet Mark III type. The C.A.V. fuel-pumps and injectors have pintle-type nozzles giving a conical fuel spray. Dry-sump lubrication is employed, and a duplex scavenge pump is used. The oil is circulated by a pressure pump at 100 p.s.i., and various relief valves are set so that large amounts of oil can still be moved when the engine is cold.

The dry weight of the engine is 1500 lb. H. C. E.

2330. New Mirrlees 16-cylinder vee engine. Anon. *Gas Oil Pwr.*, 1950, **45**, 51.—The JSS 16V engine has two banks of eight cylinders of bore and stroke 9¾ and 10½ in inclined at a 45° angle, and develops 2270 b.h.p. at 900 r.p.m. Details of the engine construction are given. Models can be made with either wet or dry sump, and measures are taken to avoid dilution of the lub. oil by fuel oil. H. C. E.

2331. Investigations into fuel injection in diesel engines. Anon. *Gas Oil Pwr*, 1950, **45**, 116–21, 135.—Describes recent experiments by Sulzer Bros. Ltd. on fuel injection.

Theoretically, the fuel should instantaneously be uniformly distributed throughout the combustion space so that each molecule of fuel would be surrounded by the number of molecules of oxygen needed for complete combustion; but since the time required for injecting, atomizing, and distributing the fuel is finite, combustion begins before the end of these operations, and the resultant rapid temp increase causes reaction of the fuel with oxygen before the fuel droplets are completely surrounded by oxygen. The injection equipment determines the quantity, nature, and distribution of the mixture before combustion, and hence the max thermal energy obtainable; and the design of this equipment presents a most complicated problem.

Two methods of investigating the problem are described. The first is to measure the distribution of the fuel entering the combustion space during the injection period, and this is accomplished by passing a row of interceptor cells across the front of the nozzle during injection. The depth of the fuel in each cell is then proportionate to the quantity of fuel ejected during the time taken for the cell to travel across the nozzle. The construction of a fuel-pump which can reproduce injection conditions over a wide range is described. The rotary interceptor system containing seventy-two cells is so arranged that each cell collects fuel over a range of 0·5° of the pump shaft. The distribution will not be entirely accurate because a smoothing-out effect is obtained, and the diagram is such that even slight fluctuations represent serious disturbances in the injection process. The diagram is also modified under practical working conditions by the pressure in the combustion space, which alters the time at which injection begins. The closing pressure of the injection needle and the temperature do not affect the diagram.

The second method is to observe the formation, development, and dispersion of the fuel-jet by stroboscopic photography. This method gives information about the form of the jet, its length, the way in which atomization occurs, and whether injection is interrupted. The apparatus by which this is achieved is described, and photographs of the jet at various time intervals are given. The development of the jet, and the discharge associated with "dribbling," in which the fuel is not sufficiently atomized for complete combustion, is clearly shown.

The results obtained by these methods of investigation have provided data from which new injection units have been designed. Attention has also been paid to the effect of the nature of the fuel on the injection characteristics. H. C. E.

2332. Performance of a large diesel locomotive. Anon. *Engineer*, 1950, **190**, 151.—Sulzer-engined twin-unit machine of 4400 b.h.p. on French National Railways has completed 1,000,000 km. in working period of 5⅔ years. Average speed 50–60 m.p.h.,

hauling passenger trains of 400–700 tons. Fuel consumption 13·4 lb/mile, lub. oil consumption 0·30 lb/mile. Mechanical wear and necessary renewals surprisingly small, *e.g.*, in a total of twenty-four pistons and forty-eight valves only two pistons and four inlet valves have been replaced. Cylinder-liners were renewed after 499,000 miles because of corrosion from cooling-water side; inside wear on liners after this mileage did not exceed 1 mm in bore of 12·2 in. A. C.

2333. Fuel injection for spark-ignition automotive engines. G. M. Lange and C. W. Van Overbeke. *S.A.E. Trans.*, Jan. 1949, **3** (1), 107–21.—The historical background of fuel injection is outlined, advantages of fuel injection are enumerated, and the units of a typical fuel-injection system are described. Details are presented of available injection systems, and it is suggested that simplified injection-pump designs, probably of the single-plunger type, will shortly be universally available. J. G. H.

2334. Calculation of the volume of rocket combustion chambers. J. Himpan. *Aircr. Engng*, July 1950, **22** (257), 191.—Previous methods of calculating volume of rocket combustion chambers employed value of "characteristic length," which must be determined experimentally for each fuel and injection system. Here, formulæ are derived giving generally valid qualitative theoretical and practical relationships between combustion-chamber volume and any desired combustion pressure, mass flow, fuel, and combustion-chamber shape. Examples are quoted to give comparisons of theoretical results with combustion chambers which have been tested in practice, including those of German V2 and American WAC-Corporal. Formula proposed also applicable, in principle, to calculation of volume of gas-turbine combustion chamber. Four references. U. N.

2335. Progress review No. 9. Developments in internal-combustion engines other than heavy-oil engines. Anon. *J. Inst. Fuel*, July 1950, **23** (132), 206.—Recent advances in engine design reflect the intensified efforts being made towards more efficient utilization of available fuels. General trend in private-car engines is to employ higher compression ratios and in buses and trucks to increase power output by supercharging. American experience has shown that under conditions of low-speed, full-throttle operation relative freedom from knocking is a function of fuel sensitivity. The possibilities of higher compression ratios are promising up to ratios of 12·5 : 1. There is some doubt whether a 12·5 : 1-compression-ratio engine will ultimately benefit user in view of higher initial cost of engine, more expensive fuel needed, and possible higher cost of maintenance. Increase of the scope of low-octane fuels by means of dual-fuel systems is discussed. In the latest high-compression engines the effects of combustion roughness have been suppressed by increasing engine rigidity. The possibility of eliminating detonation by burning the combustion mixture as it is formed has been explored. Developments in the fields of fuel injection and supercharging are discussed. "Loop scavenging" with fuel injection has eliminated the problem of fuel loss through the exhaust in two-stroke engines while retaining the inherently simple structure. An ignition process has been developed which depends on the injection of a highly inflammable liquid that ignites at the cyl temp and fires the petrol-air mixture, and it greatly simplifies control of engine output. Influence of the transmission system is also considered. Twenty-two literature references. D. K.

2336. Supercharger and the engine. R. J. S. Pigott. *S.A.E. Trans.*, July 1949, **3** (3), 473–9.—The tendencies of current engine requirements are enumerated, and the possible methods of meeting their requirements are outlined with special reference to the possibilities of the supercharger. The problem of matching the supercharger to the engine is discussed, and the Roots type and helical-screw superchargers are described in some detail with indications of performance prediction. J. G. H.

2337. High-output engines. R. J. S. Pigott. *S.A.E. Trans.*, Apr. 1949, **3** (2), 207–14.—The necessity for a high-speed indicator for examining the losses induced by design in an engine is stressed and suggestions are put forward for reducing these losses. They include rounding the inlet side of valves to raise flow coefficient, realization of the fact that the main loss in manifolds is in the bends and not in skin friction, carburettor design for as complete recovery of the throat drop in pressure as possible,

and the design of cooling jackets for a definite flow path. The possibility is discussed of getting lower octane demand for supercharged engines as compared with the single compression in the cyl for the same total amount of pressure. J. G. H.

2338. Crankcase explosions. Anon. *J. Inst. mar. Engrs*, July 1950, **62** (7), 267.—The paper consists of a report of a discussion at a joint meeting of the Diesel Engine Users' Association with the Institute of Marine Engineers. A number of authors contributed to the meeting, and the following are some of the outstanding suggestions and comments which were made. Crankcase explosions have occurred not only in internal-combustion engines but also in steam-engines of the enclosed pressure-lubricated type. There had been experiences of crankcase explosions in crosshead steam-engines when the crankcase door was removed to investigate troubles. Air was allowed to enter and form an explosive mixture, and the result was often fatal. It was suggested that an inscription should be put on crankcase doors calling attention to the use of naked lights in the crankcase after running the engine and also to the fact that if overheating of any accessible part occurred it should be allowed to cool before any casing door was opened. It has been shown in laboratory that gas in crankcase is about 90% air, so it is felt that the factor mainly responsible for crankcase explosions is the overheating of some internal part by which both inflammable vapour and means of ignition may be produced. Many other experiences are quoted, and various suggestions are made with a view to understanding the phenomenon of explosions in crankcases. A. S.

2339. Dynamically loaded bearings. M. C. Shaw. *Lubr. Engng*, Oct. 1949, **5** (5), 218–25.—The hydrodynamic theory of lubrication of the conventional journal bearing assumes invariant conditions which are frequently not encountered in practice. Such unsteady state problems are discussed, and a method is put forward which reduces each system to an equivalent conventional journal bearing for which solutions are readily available.

An hydraulic analogy is presented for the dynamically loaded bearing, and is illustrated by a detailed consideration of the operating conditions of a piston-pin bearing on a reciprocating engine. J. G. H.

2340. Engine wear research. L. D. Thompson, S. J. Backey, and E. L. Conn. *S.A.E. Trans.*, Jan. 1949, **3** (1), 41–50.—Results are presented of an investigation of engine wear, limited to wear of piston-rings and cyl bores as affected by various fuels, the procedure employed being one producing results that could be duplicated.

Work on two engines, one operating at a moderate b.m.e.p. and speed, the other at high b.m.e.p. and speed, revealed that the more heavily-loaded engine consumed three times more fuel per hr per cyl than the moderately-rated engine, and the increase in wear for a $\frac{1}{2}$% increase in sulphur was also three times that encountered in the moderately rated engine. This indicates that high rates of wear and deposits encountered at high b.m.e.p. and speeds are primarily due to the fact that more fuel is required to carry the higher loads. It is suggested that wear is caused by block abrasive deposit formed by the combination of sulphur with the hydrogen molecules of the fuel during the combustion process. J. G. H.

2341. Compounding powerplants. P. H. Schweitzer and J. K. Salisbury. *S.A.E. Trans.*, Oct. 1949, **3** (4), 656–70.—The compounding of the gas turbine and piston engine as a single power-plant is explained, and the wide range of compounded engines from the turbo-supercharged aircraft engine where the engine develops all the shaft power to the hot-gas generator plus turbine combination where the turbine develops all the shaft-power is described. Calculated performance figures are given for a power-plant with the supercharger compressor set geared to the reciprocating engine component and for the hot-gas generator plus turbine. Experimental data are given on a diesel engine used to simulate a hot-gas generator, and details are presented of a semi-free piston hot-gas generator designed to circumvent difficulties experienced with free-piston units. J. G. H.

2342. Fifty years of aero-engine and fuel development. Anon. *Airc. Engng*, July 1950, **22** (257), 197.—Review of book, " Development of Aircraft Engines and Fuels,"

by R. Schlaifer and S. D. Heron, publishers, The Harvard Business School, Soldiers Field, Boston 63, Mass., U.S.A. Book comprises two research studies, results of impartial enquiry into relationships of government and industry in development of aero-engines, covering American, British, and European experience. Influence of government in development of high-powered aero-engines and differences between American and British official policies discussed, with historical causes and effect of two systems of financing on technical development. Incentive and essential role of profit under British system, with desirability of assured market, and development of engine accessories and need for competition, are reviewed. Progress of air- and liquid-cooling of engines in America and Britain, emphasizing features of strategic and technical policy controlling respective types, and development of gas-turbines, mainly from American standpoint, are described. Review of work on carburettors and fuel-injection systems completes Part I.

Part II tells story of aviation fuel research and applications to date outlining roles of private enterprise and government, discussing competition in manufacture, engine developments, and assessment of fuel resources made, discovery of synthesized branch-chain paraffins and octane, and problems of knock and knock rating. Finally, fuel situation during war and task of organizing for war conditions are described.

U. N.

2343. Hydraulics. Anon. *Flight*, 17.8.50, **58** (2173), 191.—A brief history is given of application of hydraulics to aircraft, first for absorbing landing shock and later for actuating services. Hydraulically operated services are, in general, moved by a jack which is fed with oil from a pump. Essentials for any hydraulic system are a reservoir of oil, a pump, selector valves, suitable pipelines, and jacks to operate the individual services. A single input force is capable of moving a variety of loads, and this is achieved by arranging that area of jack piston in sq. in., multiplied by load to be moved in lb, is equivalent to pressure exerted through fluid in p.s.i. A typical modern system, as applied to a multi-engined bomber, is described and illustrated diagramatically. Connected to main pressure line from automatic cut-out is incorporated a hydraulic accumulator which accommodates some of oil fed to system at a high rate which would otherwise operate smaller jacks too quickly. Accumulator also serves as a shock absorber and as a storage of pressure. Pressure-relief valves are fitted at various points throughout the system.

Utilization of elevated pressures, and importance of reliability in civil aircraft are discussed, and application of electrical units to hydraulic components, including Power Pack system introduced by Dowty Co., reviewed. Among components described and illustrated are various types and makes of pumps, a flow divider, a steering jack of follow-up type for nosewheel steering, types of jacks and locking systems, including the collet lock.

U. N.

2344. Introduction to the comprex. F. W. Barry. *J. appl. Mech.*, 1950, **17** (1), 47–53.—The comprex is a rotary pressure exchanger, the working space of which contains alternatively hot and cold gas in order that the wall temp will remain below that which ordinary metals will withstand. The machine therefore enjoys the mechanical simplicity of the turbine and yet attains a higher thermal efficiency by allowing a higher max temp.

The construction and operation of a comprex is described, together with its application to a gas-turbine cycle. An analysis using simplifying assumptions is developed which is intended to indicate the performance characteristics of a comprex. It is shown that the pressure ratio, the relative gas flow, and the ratio of the temp of the leaving gas to that of the entering air are all functions of scavenging velocity and of the nature of the compression and expansion processes. Formulæ are given for the determination of all the major dimensions of the engine.

D. F. J.

Safety Precautions.

2345. Blueprint for an industrial safety organization plan. G. L. Farrar and A. M. Platt. *Oil Gas J.*, 27.7.50, **49** (12), 318.—The programme consists of division of plant personnel into various groups, based on functional similarities, physical locations,

organizational lines, or on any other convenient lines. Each group is then organized into a substantially independent safety group.

Three main purposes are kept in view : (1) reduction of accident hazards, (2) stimulation of safety consciousness and good housekeeping, and (3) encouragement of all employees to express thoughts on promotion of safety. G. A. C.

2346. Survey of accident prevention in industry. W. C. Sydenham. *I.P. Review*, 1950, **4**, 215.—The importance of preventing accidents cannot be stressed too much. They result in loss of money and output by the employer and possible permanent incapacity and reduction in earning power by the employee. A safety programme involves first of all the compilation of a complete detailed record of accidents, and secondly an analysis of the factors which contribute to the occurrence of these accidents. Steps should then be taken, in consultation with the Safety Officers, at all levels of works management to educate the workmen into a " safety " attitude of mind, and also to institute the necessary improvements in plant and equipment. R. H.

2347. Safety standards for work to be carried out in interior of tanks having contained crude petroleum and its products. Anon. *Bol. de Combustibles* (Argentine), 1950, **7**, 43–5.—Possible causes of accidents are listed and vapour-concn limits quoted for asphixiatory and fire risks. Severity of working conditions in tanks is classed according to temp therein, $> 35°$ C, 30–35° C, $< 30°$ C. A. C.

2348. Life and death in an oil refinery. Part 6. P. M. Van Arsdell. *Petrol. Engr*, Jan. 1950, **22** (1), C-17.—Lube oil finishing utilizes solvents, some of which are dangerous. Propane when splashed on the skin is a refrigerant and defatting agent, inhalation of the vapour has the normal hydrocarbon reactions. Phenol is a violent, rapid-acting poison on either inhalation or contact. Acute poisoning follows splashing the skin, and it has been known to cause gangrene. In the eyes it does permanent damage. Immediate first aid is copious washing and alcohol solution on the skin. Chlorene and sulphur dioxide both irritate the eyes in minute concentrations. Sulphur dioxide forms sulphurous acid with the moisture on the mucous membranes irritating the entire respiratory tract. If escape from the fumes is impossible death results. The body develops a tolerance to sulphur dioxide, but certain symptoms develop on prolonged exposure to small quantities. Ammonia acts rapidly on the eyes and lungs, and so warning is obtained of high concentrations. Eye contact is dangerous, the initial reaction is slight, but a delayed action takes place due to slow infiltration of ammonia into the eye tissue. Carbon tetrachloride is dangerously toxic on inhalation or contact, chronic poisoning results in attack on the kidneys and liver. Twenty references are given. G. K. A.

2349. Life and death in an oil refinery. Part 7. Conclusion. R. M. Van Arsdell. *Petrol. Engr*, Feb. 1950, **22** (2), C-19.—General hazards are discussed. Electrical burns should be considered serious until sufficient time has elapsed to prove otherwise. Minor electrical burns should be treated as ordinary burns, but more severe ones should have prompt medical attention. Tables are given of fatalities over the last twenty years from electric mishaps, moving machinery, ladder work, and scaffold work. When ladders are used the base should be fastened and the distance of the foot from the wall not more than one-fourth the ladder length. On scaffold work life belts are essential. 20% of all accidents are from falls, so floors, hand-rails, catwalks, and platforms should be kept clear and clean. From an examination of accident reports a large number appear to be due to carelessness. The training of safety engineers is essential and is economically sound. Reports of all accidents should be made to the management, and these should be studied to eliminate the possibility of further such accidents. G. K. A.

2350. Handling corrosive fluids, Part I. B. N. Reavell. *Fluid Handling*, Dec. 1949 (1), 17–20.—The articles cover handling, storing, and disposal of corrosive materials in chemical industry, subjects on which published data are limited.

It is recommended that materials of construction should be tested for resistance to corrosion during the pilot-plant stage as well as in the laboratory. Effluent disposal should also be included in cost estimates.

The principal safety precautions are mentioned, and references are made to more detailed rules. Problems involved in transport by road and rail, tank-cars, and carboys are discussed and solutions given. D. H.

2351. Handling corrosive fluids, Part II. B. N. Reavell. *Fluid Handling*, Jan. 1950 (2), 23–7.—Abstract No. 2350 is continued by discussion of the design of storage systems for large quantities of corrosive materials. The most suitable tank linings, pumps, and pump glands are suggested for various liquids and gases occurring in chemical industry. D. H.

2352. Simplified eye washer for general laboratory use. J. F. Corwin and R. McConigal. *Chem. Education*, Aug. 1950, **27** (8), 461.—Describes a simplified eye-washer which can be constructed easily and at little cost, although it must be admitted that it is not as efficient as the commercial product. The materials required for its construction are a rubber bulb-type toilet plunger, a few elbow joints and short lengths of small-dia water-pipe, a water-pressure regulator, and a faucet or spring valve. The plunger serves as the eye-washing cup, and is pierced through the top and inverted to fit over the small-dia pipe, which may be connected to any water source. One or two small holes are pierced at the bottom of the cup to allow water drainage while the eye is in contact with the cup. Water flow in the eye-washer cup is adjusted by a water-pressure regulator. Drawings of the cup illustrate its construction and installation. A. S.

2353. Extended pressurized safety hood allows in-place repair of ketone filters. P. C. Folse and H. T. Fort. *Oil Gas J.*, 27.7.50, **49** (12), 334.—A method for using welding, burning, or soldering in the repair of ketone filters, without their removal or loss of unit stream time as developed by the Beaumont refinery of the Magnolia Petroleum Co. is described.

The filters under repair are housed in, while keeping a positive pressure on the enclosure whilst work is in progress, after the filter has been disconnected and washed free from oil and gases. Utilities are run through rubber grommets in port openings on the hood. G. A. C.

2354. Spontaneous combustion causes tar reservoir fire. J. S. Corlew. *Refiner*, 1950, **29** (6), 121–2.—A fire, which consumed an estimated 500,000 brl of petroleum waste tar and acid sludge in earthern reservoirs on June 17, 1949, was considered to be due to spontaneous combustion. The fire was preceded by heavy rainstorms, and it is thought that the heat of dilution of the acid, together with the heat evolved by the reaction of the sulphuric acid and the tar was sufficient to cause spontaneous combustion. Fire had occurred on two previous occasions and had been extinguished. Water produced a foam which smothered the flames over a limited area, but it was not possible to produce enough foam to cover the entire surface, and piles of burning coke also provided a source of re-ignition. It was decided to let the fire burn itself out (about ten days). Fortunately the wind was in a favourable direction, for the smoke contained unburnt particles of tar and soot which might have caused damage to a neighbouring town and the refinery. Contact was maintained with the weather-reporting stations for predicted winds and velocities. R. W. G.

2355. "Bean soup" of navy fame applied to industrial plants. Anon. *Refiner*, 1950, **29** (1), 102–3.—Description of the application of mechanically-formed air foam for industrial fire protection. It is claimed that this type of foam offers advantages over CO_2 foams. R. W. G.

Miscellaneous.

2356. Imports up, exports down for first half of 1950. H. D. Ralph. *Oil Gas J.*, 27.7.50, **49** (12), 192.—Import of crude and products currently into the U.S.A. has been averaging about 220,000 b.d. more than a year ago, whilst imports have been 100,000 b.d. less.

Tables detail imports and exports of petroleum products, and compare January–May 1949 *v* 1950. G. A. C.

2357. Economic and financial development of the chemical process industries. R. S. Aries and J. W. Spence. *Industr. Engng Chem.*, 1950, **42** (6), 936–74.—A general survey of development of the chemical-process industries includes tables of assets, liabilities, capital, earnings distributed, and net income for various industrial groups. Petroleum and coal products are grouped together. An analysis of financial sales of 100 chemical-process companies includes several of interest to the petroleum world. R. G. T.

2358. Use of olefins for chemical production—1940–1950. R. S. Aries and U. Copulsky. *Oil Gas J.*, 6.7.50, **49** (9), 54.—The great growth in use of olefins for chemical production in the eleven-year period 1940–50 inclusive is shown. Most important olefins have been ethylene, butylene, propylene, and *iso*butylene.

Tables show consumption of olefins in the chemical industry, and consumption of ethylene, propylene, butylene, and *iso*butylene; also estimated value of primary products made from olefins 1950. G. A. C.

2359. Post war record and future. M. F. Grass, Jr. *Industr. Engng Chem.*, 1950, **42** (6), 974–8.—Comparison with pre-war figures is made of post-war growth of chemical-process industries grouped as in the previous paper. Tables of production prices, employment, and earnings include separate reference to petroleum and allied products. R. G. T.

2360. Organic chemicals. J. H. Hibben. *Industr. Engng Chem.*, 1950, **42** (6), 990–7.—General review of production figures of synthetic and natural organic chemicals is made for 1949, and comparison is made with previous years. Statistics are supplied for coal-tar crudes and intermediates, petroleum, and natural-gas products. R. G. T.

2361. 1949 brings about easing of industry's operations. Anon. *Refiner*, 1950, **29** (1), 69.—A review for the year 1949 of the U.S.A. petroleum industry by the A.P.I. Throughput was slightly less than for 1948. This was the first time since the beginning of the Second World War that throughput was not increased. The reduction in the demand on the industry is attributed to a decline in export requirements and to unseasonably warm weather in the winter, causing a relatively small domestic fuel-oil consumption. Refining capacity was again increased. Figures for the production of various products over the last few years are given. Total crude processed in 1949 was 5,310,000 b.d.—total crude capacity for 1949 was 6,550,000 b.d. (unconfirmed figure). R. W. G.

2362. Showdown soon on E.C.A. financing of British oil plans. H. Ozanne. *Refiner*, 1950, **29** (1), 70.—Reference is made to the British government's proposal to stop the importation of fuel oil and to cut gasoline imports to one-third in order to save dollars. The anticipated effect on U.S.A. companies is indicated. Figures for refinery developments in France, U.K., Italy, and Trieste are given, showing the proportion of the expenses borne by the Economic Co-operation Administration (E.C.A.). Figures are also given for other European countries. Reference is made to the E.C.A.s petroleum chief's statement that there is at present a surplus of petroleum crude and refined products. R. W. G.

2363. Fuel oil markets—past and future. A. J. McIntosh. *Refiner*, 1950, **29** (4), 77.—(*Condensation of study presented to Western Petroleum Refiner's Assoc.*)—Graphs and schedules give a detailed study from 1937 of the consumption of liquid fuels and forecasts are made for the period 1950–53, allowing for the effect of the expanding natural-gas and liquefied petroleum gas industries on the market. Based on present pipeline plans, it is concluded the largest effect will be felt in 1951. It is forecast that by 1953 the gasoline yield will have to increase to 46% out of the crude barrel, while the combined fuels need to drop from the 1950 figure of 44½% to below 42% for 1953,

while an even greater drop is expected for residual fuels. The overall consumption of petroleum products, however, should continue to increase, though rather more slowly, during the next few years. R. W. G.

2364. Test data meagre from five years of synthetic fuels research. V. B. Guthrie. *Petrol. Process.*, 1950, **5** (5), 505–10.—The results disclosed to date in the 1949 annual report of the Secretary of the Interior concerning the U.S. Bureau of Mines research into synthetic fuels are reviewed. Actual operating and yield data from the demonstration plants are almost entirely absent, although information on daily production, capital investment, and operating costs for a 10,000-b.d. shale oil plant is given and reproduced in tabular form by the author. Other work included in the Bureau report and reviewed consists of information on oil from coal vapour-phase and liquid-phase hydrogenation plants, gas-synthesis and related oxygen plant, plant for the hydrogenation of heavy petroleum residuums, and progress in underground coal gasification. The reports referred to are Nos. 4651, 4652, 4653, and 4564. D. W. F.

2365. Cost estimation—pipes. R. A. Dickson. *Chem. Engng*, 1950, **57** (1), 123–35.—Calculation of the cost of piping is simplified by keeping data for one size of pipe only. This figure is then converted to the cost of the same set of fittings in a different size by multiplying by the " N factor." Graphs of N factor vs. pipe size are given for a range of materials, insulations, and resistant linings. A reference cost for labour and materials is given, based on prices for July 1949. D. H.

2366. Refining trends for April, 1950. Anon. *Petrol. Process.*, 1950, **5** (5), 533–5.—Except for gasoline stocks, which are up slightly on April 1949, the major product stocks are down and were further reduced in April. Use of natural-gas liquids in motor fuel over first quarter of 1950 is 10% up on 1949 first quarter. Heating oil and residual fuels production is higher, due to demand caused by continuing cold weather over April. D. W. F.

2367. Mineral fuels. T. W. Hunter. *Industr. Engng Chem.*, 1950, **42**, 982–3.—Relative importance of coal and oil as energy sources in the U.S. is discussed. Oil consumption is increasing at a higher rate than usual. R. G. T.

2368. Fourth world power conference. G. E. Foxwell. *Nature*, 1950, **166**, 213.—Brief summary of the nineteen sections of the discussion on " World energy resources and the production of power " held in London, July 10–15, 1950.

The demand for coal and oil during recent years has been such that other methods of generating electricity are being used. In addition to hydro-electric schemes and energy from nuclear fission; windpower, volcanic heat, and a method based on the vertical temp gradient existing in tropical seas are being investigated.

In the oil industry the discovery of new reserves is more than keeping pace with present-day requirements, mainly by increasing the depth of wells and by exploiting the under-sea areas bordering the U.S.A.

The chemistry of the problems in the petroleum industry is discussed, and the application of these processes to the products of liquid fuels from brown coal, etc. Other sections describe the use of natural gas, pulverized fuel, peat, etc., in industry and in the gas turbine. H. C. E.

2368a. Oil supplies for Western Europe. Anon. *Gas Oil Pwr*, 1950, **45**, 114, 129.—American aid to the oil industries of Western European countries, the effect of devaluation on oil prices, and British oil policy *vis-à-vis* the U.S. are discussed in a newly published Congressional Report summarized in this article. (Author's Abstract.) H. C. E.

2369. Australian petroleum industry. Anon. *Petroleum*, Jan. 1950, **13** (1), 8–12.—A condensed account of a review prepared for general information by the Division of Industrial Development in the Department of Post-War Reconstruction. It examines the general demand and supply situation in the Australian oil industry. The industry

plays only a small part in providing the needed supplies of petroleum products. In all cases, except bitumen, the greater part of supply is provided by imports. Demand is rapidly increasing, and the advantages of increased home refining are pointed out.

No large deposits of crude petroleum have yet been located in Australia, although extensive oil exploration is now in progress. R. E. P.

2370. (Polish) Petroleum industry in 1948. T. Trawinski. *Nafta*, Mar. 1949, **5**, 41–6.—Analyses progress made in 1948 and in previous years and shows, with the help of tables, the increasing rate of improvement. M. S.

2371. The why, how and economics of waste-heat recovery. L. D. Stewart. *Oil Gas J.*, 13.7.50, **49** (10), 70.—The article illustrates savings possible by: (*a*) improving efficiency of a furnace; (*b*) installation of heat-exchanger; (*c*) installation of steam superheater and of (*d*) exhaust steam turbine.

A figure shows a possible power-processing flow wherein the most obvious savings from waste-heat recovery can be realised. G. A. C.

2372. Inventions and patents. Part I. A. H. Seidel and Z. D. Bonner. *Refiner*, 1950, **29** (6), 99–102.—The patent system in the U.S.A. is explained and an interpretation of many of the terms used is given.

A patent confers only the right to exclude others from making, using, or selling the patented invention for a period of seventeen years.

Any person who has invented or discovered any new and useful art, machine, manufacture, or composition of matter or any new and useful improvements thereof—and not known or used by others—or described in any printed publication—may obtain a patent.

Care should be taken by technical people in the handling of articles for publication if it is intended to apply for a patent. In defence of a patent, proof is often required that the person named is the original and first inventor. Therefore it is advisable to keep signed and dated records of all laboratory work leading to an invention.

R. W. G.

2373. Materials handling. W. J. Webb. *Auto Engr*, July 1950, **40** (529), 254.—The three fundamental elements—method, motion, and time—determine output, production cost, and the purchasing power of wages. Efficient methods, motion economy, time standards, and planned materials handling are essential in any enterprise engaged in manufacturing, processing, or distribution. The paper discusses in detail rate-fixing and time-and-motion study, and puts forward the following conclusions: (i) Time study can do little to increase productivity, except in highly repetitive or in light industries. (ii) Time study is not complementary to materials handling; materials handling alone would appreciably increase production in most industries. (iii) Motion economy and materials handling are complementary, and applied together could result in a marked increase of output. A. S.

2374. The foreman in maintenance—duties and method of grading. R. L. Rude. *Petrol. Process.*, 1950, **5** (5), 489–91. (*Meeting of A.P.I. Divn of Refining, Cleveland, May* 3, 1950.)—The difference between repetitive production of merchandise and the non-repetitive nature of refinery maintenance work is responsible for the difference in attainable efficiency between the two. It can, however, be improved by proper standardizing, scheduling, and planning of the work; in this the foreman plays a vital part. The foreman's job is analysed and a procedure, devised for his evalution with respect to capacity to develop the necessary characteristics and abilities for maintenance work is described. D. W. F.

2375. Non-domestic uses. A brief look at some out of the ordinary light oil applications. B. Dunphy. *Fuel Oil & Oil Heat*, July 1950, **9** (7), 91.—Four non-domestic uses for light oil-burners are described. Diagrams for burner installations for bake ovens show that the fire-box floor is slightly above the level where the coal grates were once located. Some installers place the firebox lower, in the former position of the ash pit. The grate area in sq. ft., divided by two gives the oil-firing rate needed in g.p.h. Oil-fired garbage incinerators eliminate odours, excessive smoke, and the

problem of obtaining quick complete combustion of wet loads of garbage. Also converting incinerators to oil nearly doubles the capacity of the plant.

Oil-burner systems used for crematoria should be capable of having their firing rate altered and be of approximately 10 g.p.h. capacity.

Horizontal rotary cup burners of midget size, vaporizing pot-type burners, horizontal flame vaporizers, and low-pressure gun burners can all be applied successfully to commercial cooking-ranges.

Other applications of light oil-burners are : use in ceiling-suspended furnace units and for portable burners which are used for temporary heat, plaster drying, tobacco curing, potato car heating, etc. D. K.

2376. A basis for fuel selection. O. G. Pamely-Evans. *Mech. World*, 11.8.50, **128** (3317), 130.—Fuels may be obtained in four physical forms, solid, liquid, or gaseous phases, and as electric power. Immediate problem which arises in the selection of a suitable fuel is convenience of application. Solid fuels have disadvantage in that they have to be handled in bulk quantities, and the solid residue or ash has to be handled in a similar manner. Ash disposal is also a difficult problem. Liquid fuels also require handling, but have no ash-disposal problem. Gaseous fuels and electricity have no ash difficulties, and are available to almost all areas without any handling requirements. As far as availability is concerned therefore piped or wired fuel supply is a great advantage. From the point of view of fuel efficiency, a chart is supplied which shows how the efficiencies of the various fuels vary with temperature when operating in a furnace. It shows that oil and coal are more efficient than coke-oven, producer, and blast-furnace gases at all temps. The effect of the dilution of fuel gases with inerts is then considered, and it is stated that the steel industry have tackled this problem by oxygen enrichment. A. S.

2377. Heating and cooling media other than water. D. G. Lewis. *Heating Ventilating Engr*, July 1950, **24** (277), 2.—The essentials of any heat-transfer medium are listed, and then a number of such liquids are examined individually to see if their physical properties are suitable. Among these are included brine, glycerine, ethylene glycol, Aroclor, Dowtherm, mineral oil, tetra-aryl silicates, and mercury. Brine is used for refrigeration purposes ; glycerine as a non-freezing solution in cooling jackets and for hydraulic testing in frosty weather ; ethylene glycol as a non-freezing solution for cooling jackets and as a high-temperature cooling liquid for aero-engines ; Aroclor 1248, Dowtherm A, tetra-aryl silicates, and mineral oils as heat-transfer media for industrial and food processing ; mercury has been used for process heating. Other solutions are given which can be used for cooling purposes, and others are suggested for low-pressure and high-pressure hot-water systems. A. S.

2378. New diffusion pump oil.—Higher monoalkyl-naphthalenes. T. Kuwata, S. Tomiyama, and M. Takao. *Bull. Chem. Soc. Japan*, 1949, **22** (2), 66–8.—The preparation of alcohols and of the dodecyl-, tetradecyl-, hexadecyl, and octadecyl-naphthalenes are described, and their properties are recorded. Japanese acid clay was employed as the dehydrating and alkylating agent in reacting the alcohols with naphthalene. The vacuum test and the oxidation test of the monoalkyl-naphthalenes, carried out in a Hickman-type diffusion oil-pump, are described. The alkyl-naphthalenes are shown to be good diffusion-pump oils, and the monododecyl-naphthalene gave the best performance with regard to the action of the pump at low temperatures. The high attainability of vacuum are :—

Monododecyl-naphthalene	$2{\cdot}1 \times 10^{-6}$	mm-Hg.
Monotetradecyl-naphthalene	5·2	,,
Monohexadecyl-naphthalene	4·5	,,
Monooctadecyl-naphthalene	1·2	,,
" Kao " oil	3·0	,,

The oils are very resistant to oxidation. W. H. C.

2379. Nomenclature of petroleum. Anon. *Bol. de Combustibles* (Argentine), 1950, **7**, 43.—South American Institute of Petroleum has recommended that vol of pet

products should be expressed in m^3 (at 15° C), and that when quantities are given in tons sp. gr. 15/4° C should be indicated. Definitions, which are suggested for official use in S. America, are given for seventeen main groups of pet products from natural gas to pet coke. A. C.

2380. Use of bacteria studied as measure of stream pollution by wastes. Anon. *Petrol. Process.*, 1950, **5** (5), 498–9.—A condensed version is given of a paper presented at the 15th Mid-Year Meeting of the A.P.I. Division of Refining, Cleveland, May 3, 1950, entitled "Use of bacteria as test organisms in stream-pollution studies," by W. B. Hart, based upon a report of the author's of an A.P.I. research project to determine what forms of bacteria could be used as test organisms in measuring stream pollution, and how such tests should be conducted. The biological survey of a polluted stream is being used to establish a record of its condition before and after waste treatment, although no single form of bacteria is sufficiently characteristic of polluted or clean water. The use of other test organisms, such as aquatic life, diatoms, and fish, are discussed. D. W. F.

2381. Disposal of colliery sludge and slurry. Anon. *Fluid Handling*, Dec. 1949 (1), 15–16.—The methods available for conveying liquids with a high percentage of fine solids are compared in three examples. Manual and mechanical labour was found too expensive compared with the use of the Mono slow-running sludge pumps. The ram type of pump was also inferior to the Mono in the case of handling a near-solid gritty material. D. H.

2382. The importance of the preservation and packaging of equipment for the oil industry. D. A. S. Williams. *J. Inst. Petrol.*, 1950, **36**, 309–35.—The operations of oil companies depend on their materials being delivered to the site in first-class condition. Bad packaging accounts for a proportion of the damage and loss which does occur. The commonest causes and the extent of the true loss are examined. An outline is given of a theory for determining the economic cost of packaging. The need for development of technique, of statistical data on which calculations can be based, and for scientific packaging are stressed; lines of approach to these problems are suggested. A. R. W. B.

BOOK REVIEWS.

The Properties of Asphaltic Bitumen. J. P. Pfeiffer. New York: Elsevier Publishing Company, 1950; London distributors: Cleaver-Hume Press. Pp. xvi + 285. 45*s*.

Although inspired by Dr J. P. Pfeiffer this, the latest volume in Elsevier's Polymer Series, has the advantage of having been compiled by a number of collaborators, including Prof. H. Eilers, Dr R. N. J. Saal, and Messrs Labout, Siegmann, and Slotboom.

The volume sets out the results of some very extensive scientific and technical research by the Royal Dutch Shell Laboratory having as its main object to describe in detail the composition and structure of asphaltic bitumens and to record those properties on which their technical application depends as revealed by scientific research. The authors set out to discuss the properties of asphaltic bitumens with particular reference to their technical application, and they achieve this object at a very high standard.

Following an introductory chapter dealing with definitions, nomenclature, and concepts, the constitution of asphaltic bitumens is then discussed in detail, first, from a chemical, and secondly, from the colloidal point of view. The physical properties of asphaltic bitumens are then dealt with, and under this heading the rheological properties are discussed in considerable detail followed by surface phenomena, thermal and electrical properties, etc. This section of the book is of a particularly high standard, and will undoubtedly prove to be of considerable value.

A short chapter on chemical reactivity is followed by one dealing with the manufacture of asphaltic bitumen. The next section dealing with methods of routine

investigation is usefully divided into : (*a*) properties commonly considered as relating to the quality of the bitumen and (*b*) tests which are generally assumed to bear no direct relation to the use of asphaltic bitumens for various applications, but which are of importance for their identification. Although quite comprehensive it is a little unfortunate that in this section more reference is not made to the British work particularly to the methods standardized by the Institute of Petroleum and the British Standards Institution. For example, it is somewhat surprising to read that according to the authors the three solvents which are recommended for extraction of bitumen from mixtures with mineral aggregate are carbon disulphide, benzene, and chloroform. It is doubtful if any British workers ever use chloroform for this purpose to-day, whilst on the other hand, it is curious that there is no reference to trichlorethylene in this connexion.

Subsequent chapters deal with special forms in which asphaltic bitumen is processed and include a discussion of properties of asphaltic bitumens in the light of their technical applications. Adequate author and subject indexes are included.

Although the book is of a high scientific standard and may by some be considered in parts academic, the technological significance of all the work carried out is clearly indicated and is obviously to the forefront in the minds of the authors throughout their work. For example, in discussing the constitution of the bitumen, it is clear that the authors' aim is to discover the causes of the variations in the properties of the material and the means by which such desired properties may be imparted to it during manufacture. Similarly, the rheological studies have supplied fundamental knowledge necessary to the selection of the most suitable grade of bitumen for a specific purpose and have also led to much clarification of the significance of routine tests and more apt interpretation of results obtained with them.

The book is well produced, and the authors are to be congratulated on the production of a volume which should be in considerable demand in all laboratories concerned with the use of asphaltic bitumens in any form, either from the point of view of manufacture or technical application. D. C. B.

Applied Sedimentation. A Symposium Edited by Parker D. Trask. London : Chapman & Hall Ltd., 1950. Pp. xi + 705. 40*s*.

" The symposium considers the practical applications of sedimentation. It is designed (1) to describe aspects of mutual interest to the geologist and to the engineer so that each can understand the other's problems and thus co-operate more effectively in their work ; (2) provide information for the consulting geologist who may not be completely familiar with specific problems ; and (3) acquaint students with the many practical applications of sedimentation so that they may be more fully informed as to possibilities for a career in this field. Each chapter is a summary of a comprehensive subject." This quotation from the preface to the above book states the objectives which have been considered in preparation of the symposium and the Editor and authors are to be congratulated in having produced a volume which meets the widely differing needs of the geologist, field engineer, and student. The book is divided into seven parts, respectively (1) Basic principles of sedimentation ; (2) Engineering problems involving strength of sediments ; (3) Applications of processes of sedimentation ; (4) Applications involving nature of constituents ; (5) Economic mineral deposits ; (6) Petroleum geology problems ; (7) Military applications. Each part contains a number of chapters, or more properly review articles, written by different contributors and each contributor is a recognized expert in the subject of his review. In all thirty-five articles are included, each of which reviews a particular subject up to the end of 1949. Rather than duplicate material of more or less common knowledge to geologists the problems of petroleum geology, part six, have been restricted to three topics of current interest, namely, " Subsurface techniques " by Daniel A. Busch, " Porosity, permeability and capilliary properties of petroleum reservoirs " by Charles A. Russell and Parke A. Drakey, and " Carbonate porosity and permeability " by W. C. Imbt. Each of these articles is written primarily as an introduction to the subject using a historical approach which covers briefly the subject-matter from the earliest to the most recent developments. As in all other articles an extensive bibliography is given which will facilitate a further study of the subject.

The book provides a similar introduction to almost all branches of engineering which have any connexion with sedimentation. In addition to problems involving the

strength of sediments, such as highway engineering, foundations, dams, soft-ground tunnelling, landslides, soil conservation, etc., chapters are included on the composition of clays in the field of ceramics, foundry sands, sedimentary iron deposits, and applications to military and naval problems.

It might be expected in view of the wide range of subjects covered that the individual chapters would tend to become mere compilations of references. This is not the case, and in most chapters the number of actual references cited in the text is very small. For this reason books and journals as well as articles are included in the bibliography. Care has been taken to ensure that the chapters, whilst revealing individual character, should conform to a general plan of presentation. The result is a thoroughly pleasing book, of considerable value to geologist, engineer, and student. F. M

APPLICATIONS FOR MEMBERSHIP OR TRANSFER.

October 1950.

The following have applied for admission or transfer to the Institute. In accordance with the By-laws, the proposals will not be considered until the lapse of at least one month after the publication of this *Journal*, during which time any Fellow, Member, or Associate Member may communicate by letter to the Secretary, for the confidential information of the Council, any particulars he may possess respecting the qualifications or suitability of the candidate.

The object of this information is to assist the Council in grading the candidate according to the class of membership.

The names of candidates' proposers and seconders are given in parentheses.

Applications for Membership.

Blott, John Frederick Thomas, chemist, "Shell" Refining & Marketing Co. Ltd. (*W. R. P. Hodgson ; G. W. Dorrell.*)

Bookey, John Terence Brownrigg, technical manager, Messrs. Charrington, Gardner, Locket & Co. Ltd. (*D. J. Heslop ; W. A. Hubbard.*)

Cunliffe, Harold, manager (Fuel Oil Dept.), Shell-Mex & B.P. Ltd. (*C. T. Brunner ; R. J. Bressey.*)

Cushing, Antony Henry Shelley, Captain, R.A.S.C. (*R. E. Griffiths ; E. F. W. Peberdy.*)

Hughes, Fred, assistant chief chemist, Manchester Oil Refinery Ltd. (*E. J. Dunstan ; G. H. Harries.*)

Kiell, Francis James, ship surveyor, Hong Kong Government.

McIntosh, Henry James, assistant chief chemist, Standard Motor Co. Ltd. (*N. A. Clegg ; G. H. Harries.*)

Nolan, Jack, sales engineer, Regent Oil Co. Ltd. (*E. V. Paterson ; W. A. Webster.*)

Penzias, Walter, research engineer, "Shell" Refining & Marketing Co. Ltd. (*C. D. Brewer ; E. T. Hutt.*)

Secker, Reginald Louis, Flight Lieutenant, R.A.F. (*R. J. E. Walker ; G. Sell.*)

Smith, John Leslie, laboratory assistant, "Shell" Refining & Marketing Co. Ltd. (*D. H. Japes ; P. S. Stephinson.*)

Webber, William Gerald, engineer, Korea Oil Storage Co.

Wright, Lawrence Dudley, senior assistant chemist, "Shell" Refining & Marketing Co. Ltd. (*D. H. Japes ; N. E. Jones.*)

Transfer.

Mayo, Frank, petroleum engineer, Anglo-American Oil Co. Ltd. (*G. Noble ; P. Kerr.*)

NEW MEMBERS.

The following elections have been made by the Council in accordance with the By-Laws.

Elections are subject to confirmation in accordance with the By-Laws.

As Fellow.

GODFREY, R.

As Members.

EVANS, W. H. KEEVIL, P. W.

As Associate Fellow.

BEAUMONT, F. N.

Transferred from Associate Member to Associate Fellow.

DE PASS, P. H. H.

Transferred from Student to Associate Fellow.

WALKER, S. T.

As Associate Members.

HELLER, S. K. JOHNSON, S. JOHNSON, R. M.

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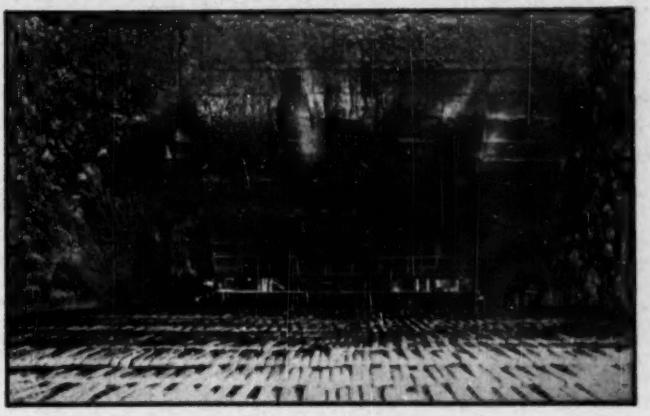

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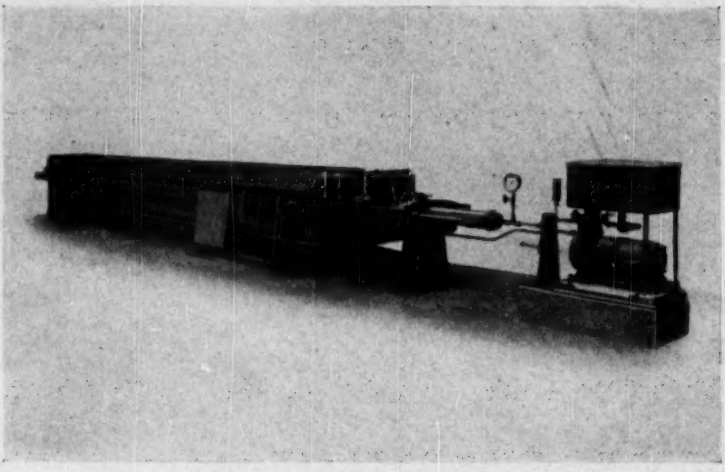

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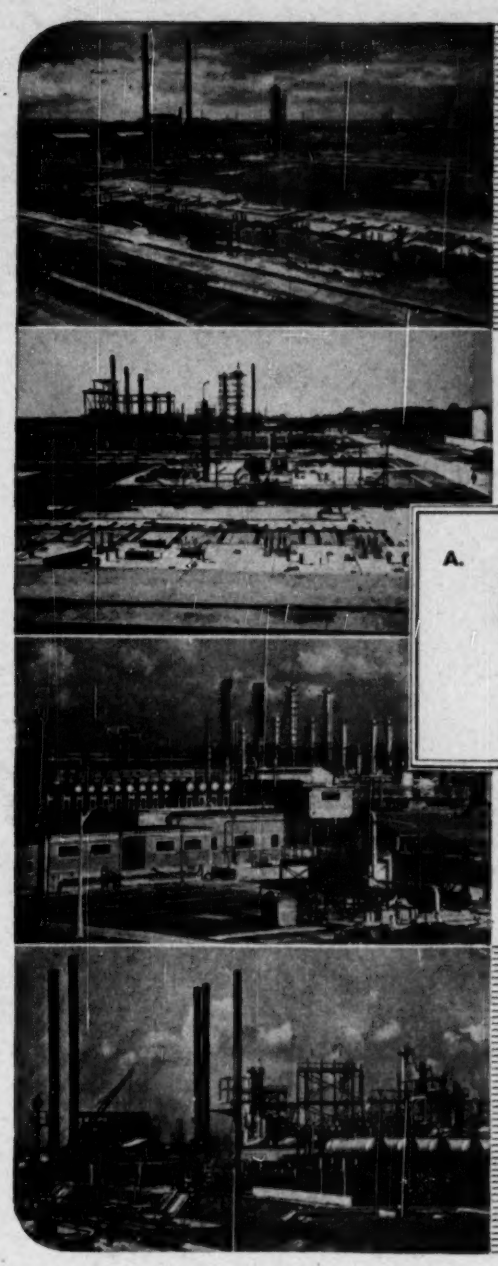

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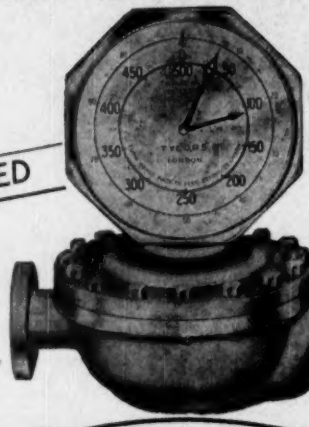

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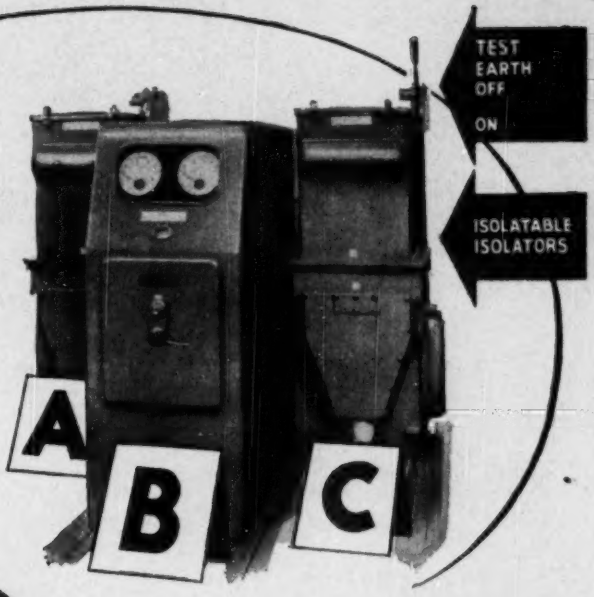

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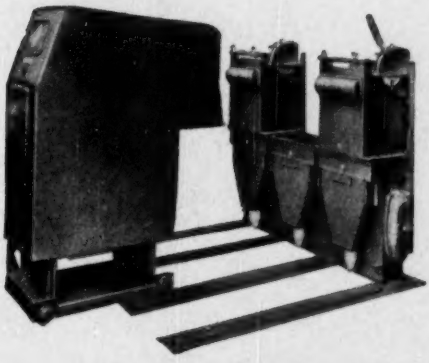

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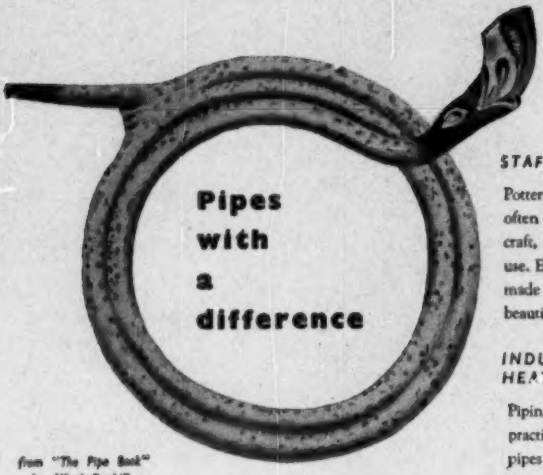

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Pottery and porcelain manufacturers have often used the pipe as a subject for their craft, for ornament rather than practical use. Elaborate coiled or snaked pipes were made of Staffordshire ware, of which a beautiful specimen is shown.

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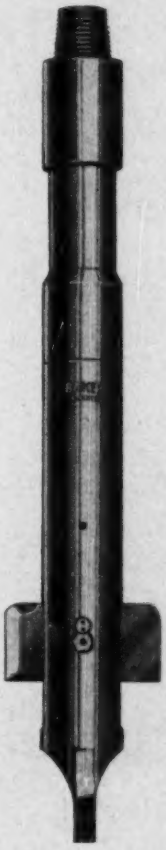
The Safety of the Baker Wall Scraper has been ably demonstrated in thousands of successful runs made in oil fields throughout the world under most adverse operating conditions.



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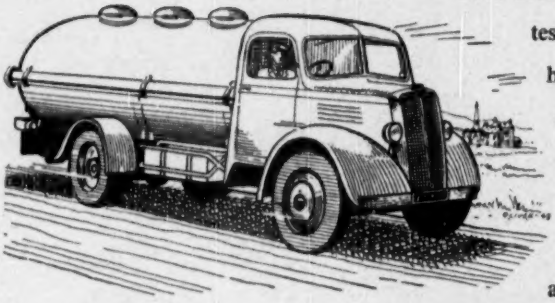

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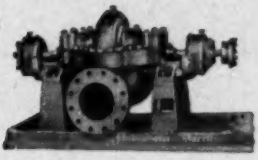

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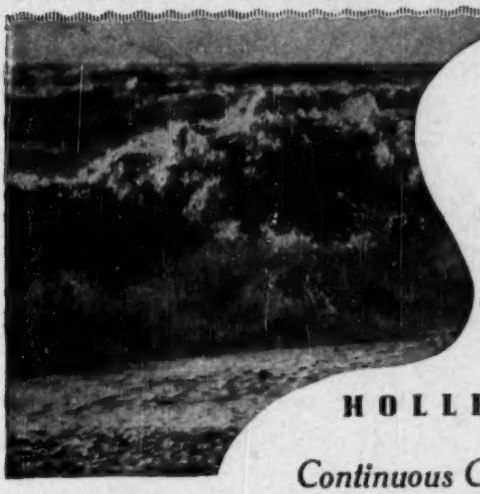

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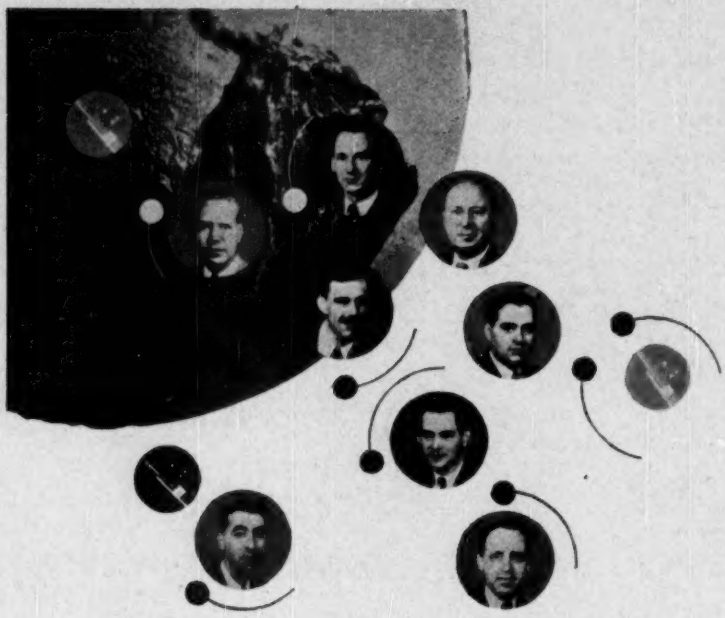

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His background is worldwide. Currently, he is at work in England, Egypt, France, Sweden, Venezuela, and across the United States. He serves on technical committees, lectures on refinery and chemical engineering practice, and writes technical papers. His viewpoint is broad and practical.

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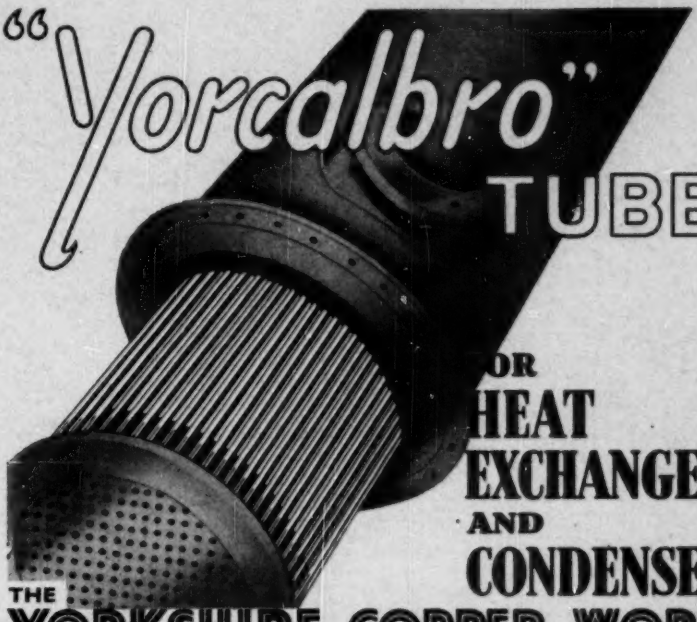

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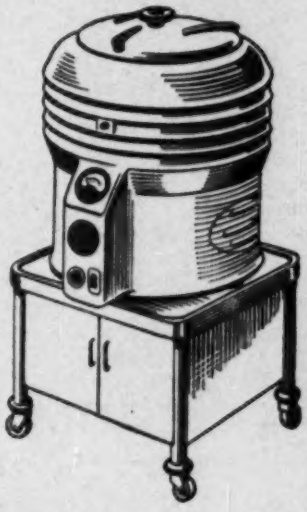

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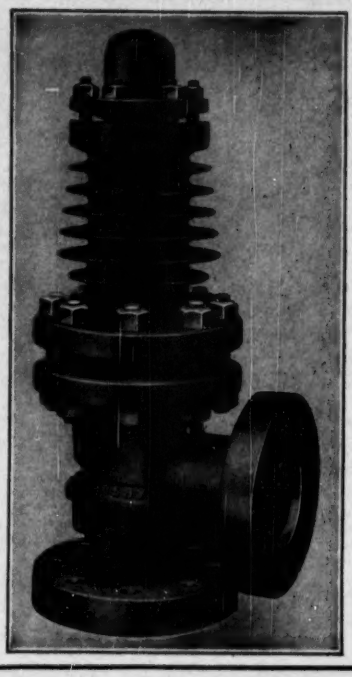

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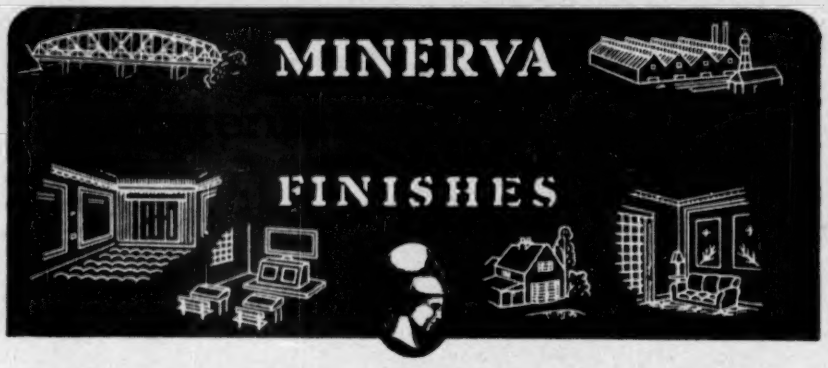

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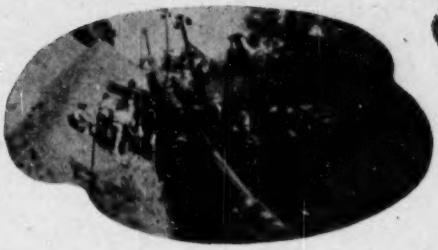

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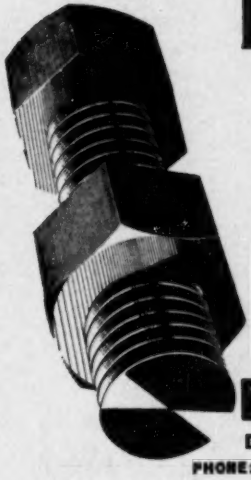

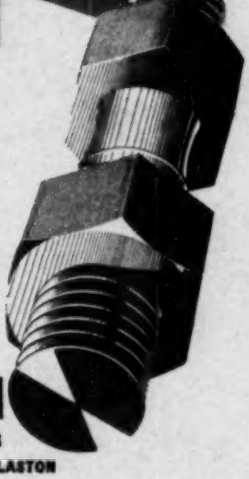

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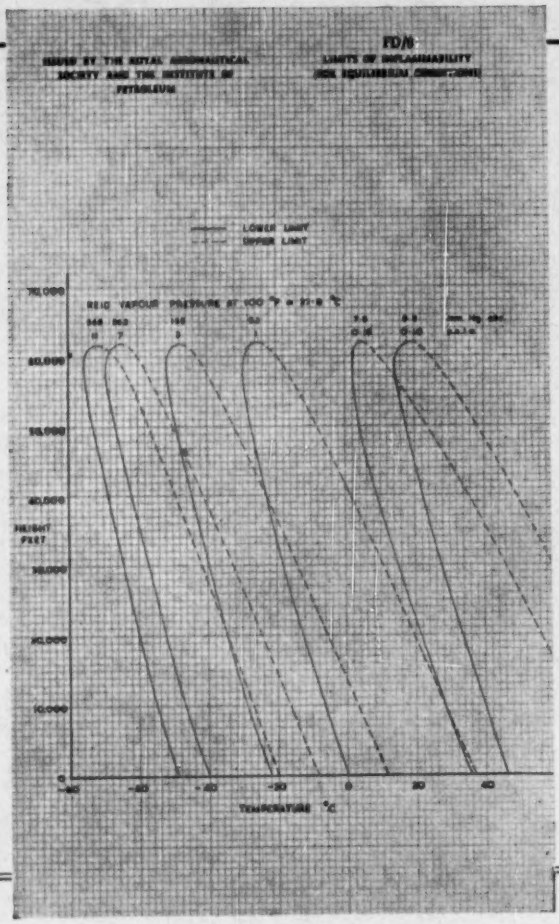

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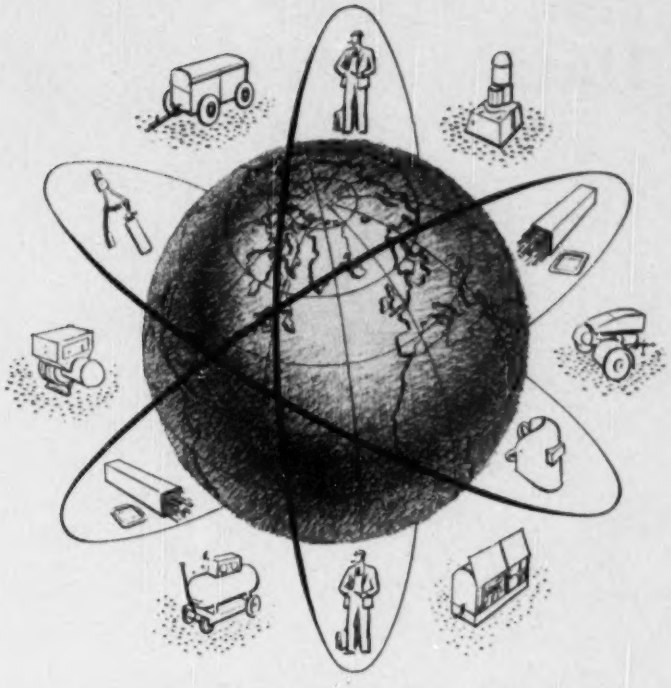

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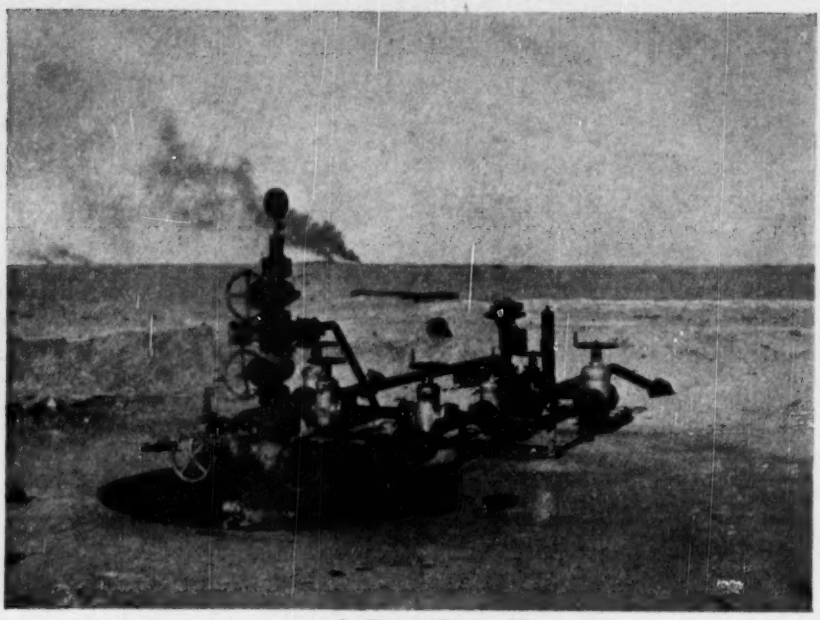

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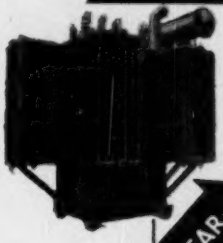

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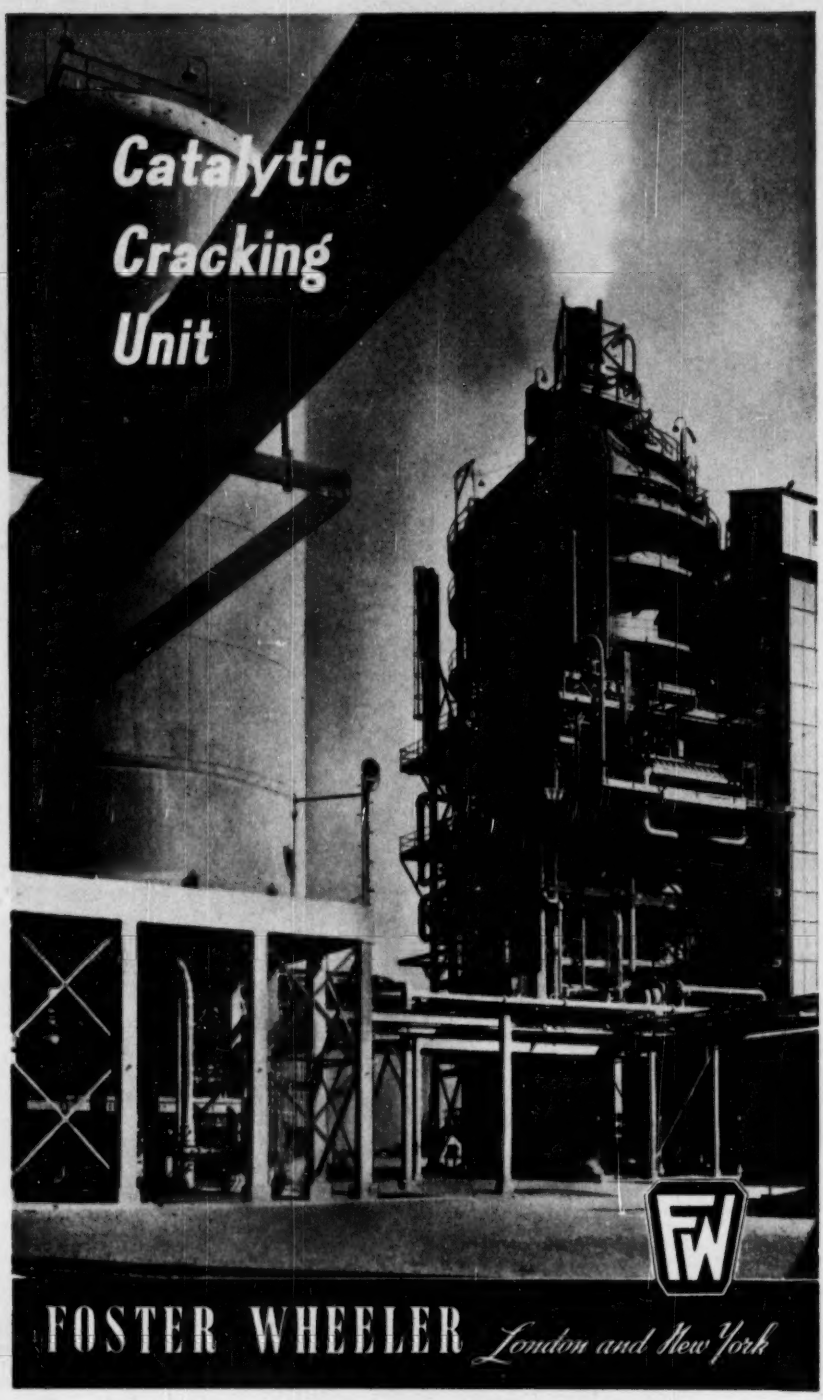

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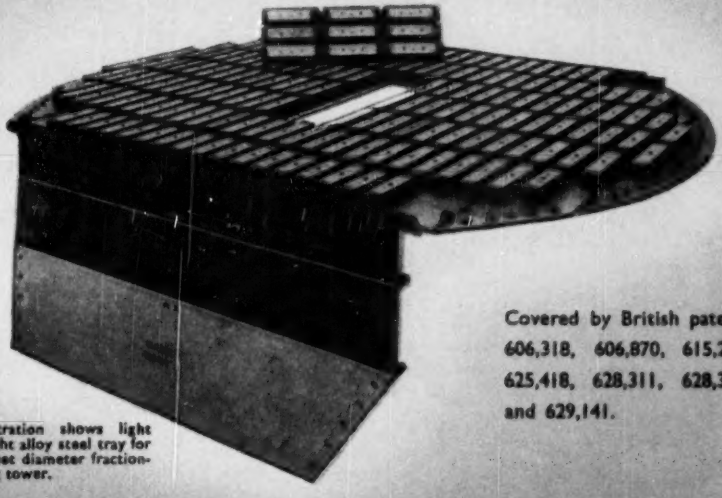

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